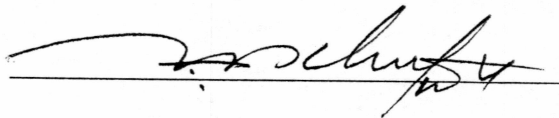


EXPERIMENTAL STUDY OF SOLID DEPOSITION AND VAPOR PRESSURE
IN GAS-TO-LIQUID AND CRUDE OIL MIXTURES FOR TRANSPORTATION
THROUGH THE TRANS ALASKA PIPELINE SYSTEM.

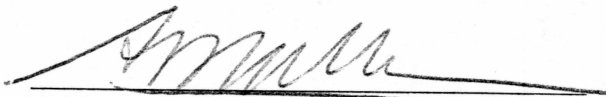
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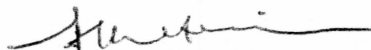
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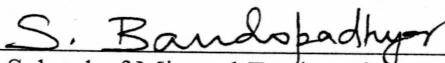


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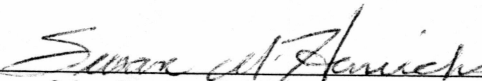


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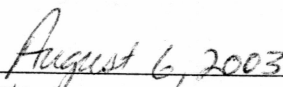
APPROVED:



Dean, School of Mineral Engineering



Dean of the Graduate School



Date

**EXPERIMENTAL STUDY OF SOLID DEPOSITION AND VAPOR
PRESSURE IN GAS-TO-LIQUID AND CRUDE OIL MIXTURES
FOR TRANSPORTATION THROUGH THE TRANS ALASKA
PIPELINE SYSTEM**

A
THESIS

Presented to the Faculty
of the University of Alaska Fairbanks
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

By

Samuel Uche Amadi, B.Eng

Fairbanks, Alaska

August 2003

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ABSTRACT

Chemical conversion of Alaska North Slope (ANS) gas to liquid and subsequently transporting it through the Trans Alaska Pipeline System (TAPS) is a means of bringing the ANS gas to the market. However, transporting the Gas-To-Liquid (GTL) product with ANS crude oil through the Trans Alaska Pipeline System (TAPS) may pose some operational challenges. The major issue of concern relates to the Asphaltene and Wax deposition problems in the pipeline, as well as the Vapor Pressure of GTL and GTL/crude oil blends.

In this study, experiments were carried out to determine the degree to which GTL is a flocculant of Asphaltene. The stability/instability of the ANS crude to Asphaltene deposition, as well as the wax appearance temperature of various cuts of GTL and GTL/Crude oil blends were also determined. The results show that GTL is a possible flocculant of Asphaltene, however, ANS is stable to Asphaltene deposition. The results also show that GTL has a high Wax appearance temperature, which raises a concern under arctic conditions.

The Reid Vapor Pressure test results from this study show no consistent trend. This is because the GTL samples used have been flashed already as a result of sample withdrawal from the container by previous researchers. Thus the sample did not meet both the ASTM and IP requirements for Reid Vapor Test.

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ACKNOWLEDGEMENTS

I would like to express my sincere thanks to my advisor, Dr. Abhijit Y. Dandekar, and co-advisor, Mr. Shirish Patil, for their relentless guidance and expert advice throughout the course of this research. I highly appreciate my committee members, Dr. Godwin A. Chukwu and Dr. Santanu Khataniar for their valuable supervision and encouragement.

I also acknowledge the U.S. department of Energy, and the Petroleum Engineering Department of UAF for their financial support. Special thanks goes to Mrs. Felicia Chukwu and her team at Alyeska Pipeline Service Company, for providing the crude oil samples and running the RVP tests. To Mr. Bill Krause of the Hazardous Materials Section of UAF Facilities Services, I say thank you for your assistance in transporting the samples to and from UAF.

My thanks are also to my pastor, Pastor Robert Harris and to my friends Dr. John Hughes and Mr. Thomas Onyekwelu for their care. To God who gave me life and strength, I give all the praise and glory.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Alaska North Slope (ANS) has a proven and recoverable gas reserve estimate of 38 trillion standard cubic feet (TCF). In addition to the proven reserve, the various fields have an undiscovered gas reserve estimate, which ranges from 64 trillion standard cubic feet to 142 trillion standard cubic feet.

This huge gas reserve has low intrinsic value because of its location, which makes its transportation to the point of use expensive. The concern of many researchers have been on how best to enhance/upgrade the intrinsic value of Alaska North Slope (ANS) gas, thereby making its transportation and utilization economically viable. Their findings (Robertson et al 1996, Liu 1999, Ramakrishnan 2000) favor the chemical conversion of these gases into liquid (GTL), and subsequently transport them through the existing Trans Alaska Pipeline System (TAPS). This option has three primary purposes namely: -

- Bring value to the product
- Bring the product to the market
- Prolong the operational life of the Trans Alaska Pipeline System (TAPS)

GTL transportation through the pipeline, however, will be faced with some operational challenges, bearing in mind that the pipeline was originally designed to transport crude oil only. Amongst these challenges is solid (Wax and/or Asphaltene) deposition in the pipeline as a result of GTL and/or GTL-Crude oil blends transportation.

Currently there are three possible modes of transportation for GTL and GTL/Crude oil blends through the Trans Alaska Pipeline Systems (TAPS). These modes are: -

1. Commingled mode (Single liquid Phase)
2. Batch mode (Two liquid phase with pigs in between)
3. Commingled Batch mode (Three liquid phases)

In commingled mode, GTL and crude oil are blended and sent through the pipeline as a single liquid phase. While in Batch mode alternate batches or slugs of GTL and Crude oil are transported through the pipeline as separate slugs with pigs in between them. In commingled Batch mode, alternate batches/slugs of GTL and crude oil are transported through the pipeline as separate slugs without pigs in between, which results to three liquid zones in the pipeline, namely: - a) Crude oil zone b) Interface or commingled zone, and c) GTL zone. The commingled zone will be at the leading and trailing edges of the slugs.

As a result of the great potential of GTL option, a three-year comprehensive research is being carried out in the Department of Petroleum Engineering, University of Alaska Fairbanks. United States Department of Energy (USDOE) funds the project, and the aim of the research is to evaluate the Operational Challenges in Gas-To-Liquid (GTL) transportation through the Trans Alaska Pipeline System (TAPS). As part of the project, this study is embarked upon with the following objectives:

1.2 OBJECTIVE OF THE STUDY

To experimentally determine: -

1. The Asphaltene content of Alaska North Slope crude.
2. The Onset of Asphaltene flocculation of ANS crude, using GTL as a flocculant.
3. The stability/instability of ANS crude to Asphaltene deposition, using flocculation Onset Titration.

4. Wax Appearance Temperature of GTL and GTL/Crude oil blends.
5. Reid Vapor Pressure of GTL and GTL/Crude oil blends
6. In addition to the above measurements, this study will also assess the impact of the measured properties on GTL and GTL/Crude oil transportation.

CHAPTER 2

LITERATURE REVIEW

This chapter reviews previous works pertinent to the work presented in this study. Background knowledge of previous work in this field is important to make the study complete in all respects.

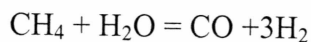
2.1 GAS-TO-LIQUID (GTL) TECHNOLOGY: AN OVERVIEW

Gas-To-Liquid (GTL) conversion, as shown in figure 2.1, is essentially a three-step process, namely: -

- i. Synthetic Gas (Syngas) Production
- ii. Synthetic Crude (Syncrude) Production or Heavy Paraffin Synthesis (HPS)
- iii. Heavy Paraffin Conversion (HPC)

2.1.1 Synthetic Gas (Syngas) Production

Syngas is a mixture of carbon Monoxide and hydrogen. It is produced by converting desulphurised natural gas into synthetic gas (Syngas), through steam reforming (SMR), partial oxidation (POX), or autothermal reforming. Steam reforming is the most commonly used conversion process and could theoretically produce synthesis gas with an H_2/CO ratio of about 3.



However, as a result of the occurring CO-shift, more H_2 is produced and the H_2/CO ratio will be in the range of 5-7 rather than 3. This results in consumption of less gas

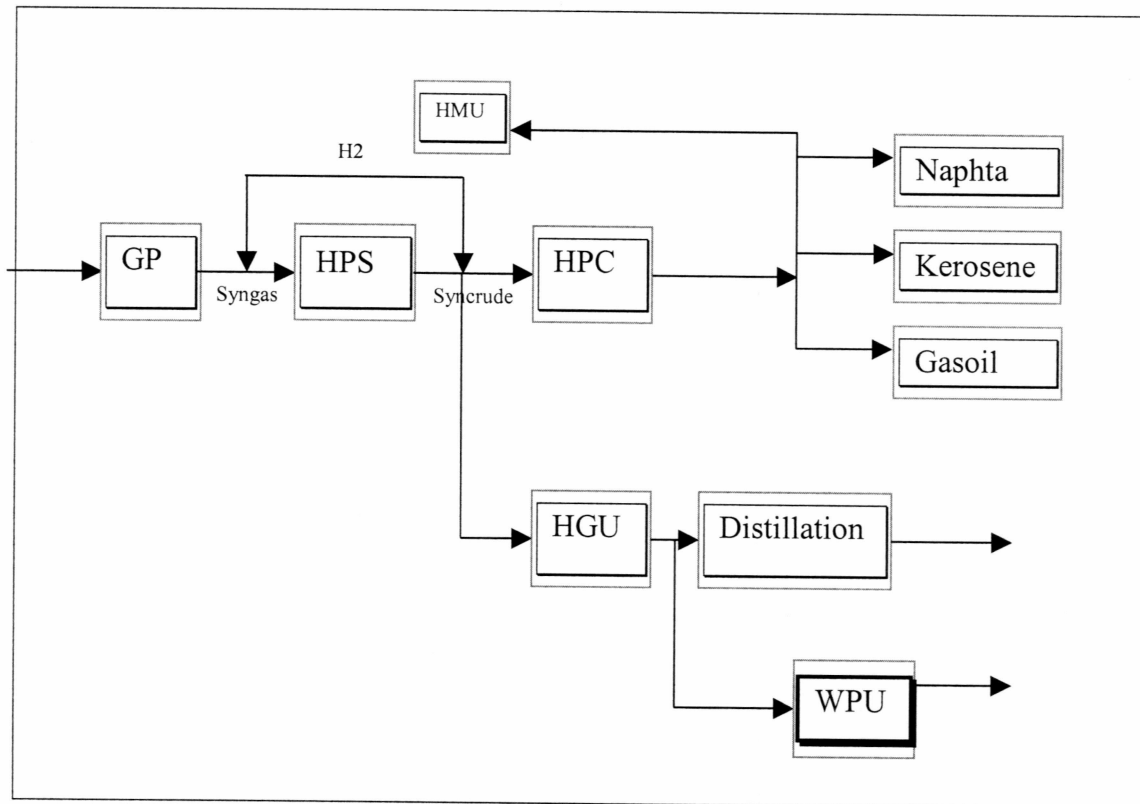


Figure 2.1 Simplified GTL Process flow scheme expected in North Slope

DsNG : Desulpherised Natural Gas

GP : Gasification Process

HPS : Heavy Paraffin Process

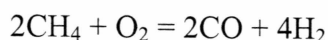
HMU : Hydrogen Manufacturing Unit

HPC : Heavy Paraffin Conversion

HGU : Hydrogenation Unit

WPU : Wax Production Unit

than is produced. The ideal molar ratio of hydrogen to carbon monoxide is just below two (Cork, M. J. 1998). Partial oxidation (POX) is the second major technology used for production of Syngas.

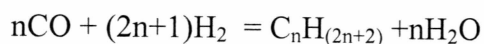


The H_2/CO ratio is about 2 and without much correction, the gas is suitable for the production of middle distillates. The oxidation is carried out with pure oxygen.

Auto thermal reforming is a hybrid process, which concurrently reacts natural gas with steam and oxygen in the optional presence of carbon dioxide (Cork M. J. 1998)

2.1.2 Synthetic Crude (Syncrude) Production

This is an exothermic polymerization reaction, which converts Syngas into paraffinic and olefinic hydrocarbons of varying chain lengths. The reaction mechanism is characterized by the probability of chain growth versus chain termination. The most common conversion process is the Fisher-Tropsch process. This process is conducted in FT reactors, which include fixed bed, fluidized bed, and slurry bed reactors. Fixed bed reactor is used primarily to produce diesel while the fluidized bed reactor is used to produce gasoline. Catalyst used in this process is typically iron or cobalt based catalysts. The process temperature ranges from 200°C to 300°C , while pressure ranges from 10 bar to 40 bar (Corke M. J., 1998). At this stage, the chemistry of the reaction is represented thus: -



2.1.3 Heavy Paraffin Conversion (HPC)

Heavy Paraffin Conversion is a mild trickle-flow hydrocracking process operating typically at 30 to 50 bar total pressure and a temperature of about 300 to 350°C (Eilers et al, 1990). Four functions are actually performed at this stage, namely: -

- i. Hydrogenation of the olefins present in the FT product
- ii. Removal of the primary oxygen-containing compounds, mainly alcohols
- iii. Hydroisomerization, and
- iv. Hydrocracking of the n-paraffins to isoparaffins of the desired chain length and or boiling range (Eilers et al, 1990)

Heavy Paraffin Conversion process is developed to selectively convert the heavy paraffins into the desired middle distillates, kerosene and gas oil.

2.2 Benefits of Gas-To-Liquid (GTL) Technology

2.2.1 Product quality

GTL is a clean product free from impurities such as nitrogen and sulphur, and from aromatic species. It has excellent cetane number and smoke point, and low particle emissions. High cetane number indicates the ease with which the fuel will auto-ignite, and how evenly it will combust. It also indicates a reduction in the formation of oxides of nitrogen (Nox), which are major contributors to the formation of urban smog and ground level ozone.

2.2.2 By-Products from GTL

i) Nitrogen

Some GTL processes use an air separation process to produce oxygen. This process also produces 2.3 times as much nitrogen, which is a very good inert gas for pressure maintenance in a depleting oil reservoir, with the added advantage that it will not cause downhole corrosion, as CO₂ will. Also it can be used in miscible flooding.

ii) Heat

GTL plants produce large amount of waste heat, therefore integration of combined cycle electric generation with a GTL plant will not only improve the energy efficiency of both processes, but will also reduce the amount of natural gas used to fire the turbines, thereby reducing the amount of CO₂ that goes into the atmosphere from the CO₂ contained in the natural gas.

2.2.3 Utilization of Remote Natural Gas Reserves

Chemical conversion of these remote natural gases, of which Alaska North Slope (ANS) gas is one, to liquid (GTL) will improve their intrinsic value, thereby making their transportation and utilization economically viable, and will also reduce gas flaring and its attendant consequences.

2.2.4 Operational Life of Trans Alaska Pipeline

GTL transportation through the Trans Alaska Pipeline System (TAPS) will extend the operational life of the pipeline to at least 25 years (Remote Gas Strategies, 1998)

2.3 GTL Transportation through TAPS

2.3.1 Transportation Modes

Transportation of both GTL and Crude oils through the Trans Alaska Pipeline system (TAPS) can be achieved by either of these three modes: -

- i. Commingled Mode (Single liquid phase)

- ii. Batch Mode (Double liquid phase with pigs in between)
- iii. Commingled-Batch Mode (Triple liquid phase)

Commingled Mode

In this mode of transportation, the crude oil and GTL are blended into a single liquid phase before being sent through the pipeline. From the tests already conducted by the Petroleum Engineering Department at University of Alaska Fairbanks, on samples of crude oils and GTL (Ramakrishnan, 2000), it was observed that both fluids blend into a single homogeneous liquid when mixed. It should be pointed out at this point that commingled mode increases direct contact between GTL and Crude oil, which directly translates into higher contamination of GTL products by sulfur, waxes, and other impurities from crude oil.

Batch Mode

This involves the use of physical barriers called pipeline pigs to separate products. The work of Baum J.S., 1998 shows that this process increases the level of contamination by creating additional turbulence. Also the use of pigs in a pipeline like the Trans Alaska Pipeline System (TAPS) will entail the removal of the pigs at each pump station, since they cannot pass through the valves. This increases operation time and cost, especially when there are up to twelve pump stations.

Commingled-Batch Mode

Commingled-Batch Mode is the process whereby alternate batches or slugs of crude oil and GTL are transported through the pipeline. There is no pig in between the slugs, and it results in the creation of a commingled interface between the fluids. The extent of commingling, or the length of the interface is a function of velocity, density difference between the two fluids, viscosity, pipe diameter, and distance traveled (Baum et al 1998).

Commingled batch process, requires that interface detectors must monitor the fluid movement, this is to minimize loss of product value. These detectors include:

Densitometer

Densitometer measures the specific gravity of the fluid. As the density varies, the fluid alters the vibrating mass, which in turn changes the resonant frequency. The output signal is then transmitted and processed without loss of accuracy with the latest microprocessor techniques.

Sound Velocity Interface Detector

This employs changes in the sound velocity to detect different liquids. At a constant temperature and pressure, sound travels through a liquid at a unique, repeatable speed. A change in the liquid composition results to change in sound velocity. The sound signature associated with each petroleum fluid makes it possible to differentiate two liquids that have almost identical densities.

Continuous Colorimeter Detector

It measures color quality with a dual wavelength, dual-detector optical system. Measurement is done continually drawing samples from the main process flow and passing a single halogen beam through the sample stream. Upon exiting the sample stream, the return beam is split and passed through optical filters. Two independent photo detectors measure the intensity of the reference and measurement beams. The signals are then translated into a color measurement by a computer.

2.3.2 GTL Transportation Challenges

To transport GTL products with crude oils either by batching or blending, a number of challenges need to be taken care of. These challenges include: -

- i. Effect of solid deposition (wax and or Asphaltene)
- ii. Effect of cold temperature on GTL with respect to cold restart.

- iii. Impact of GTL on corrosion inhibitors
- iv. Pressure losses within the system.
- v. Storage facilities for fluids at both ends of the pipeline
- vi. GTL contamination by impurities from crude oil
- vii. Heat loss within the system
- viii. Vapor pressure of GTL and GTL-Crude oil blends
- ix. Effect of GTL on internal monitoring devices
- x. Current system capabilities to handle GTL considering the pipeline were originally designed to handle a single liquid.

The focus of this study is on solid deposition therefore attention will be placed on those factors that affect solid deposition.

2.4 Solid Deposition

Solid Deposition problem means different things to different people because of the variation in vantage points related to solid deposits engineers and researchers have. For instance, for the reservoir engineer it may mean formation damage and in-situ plugging; for the production engineer, near well formation damage and subsurface and surface equipment plugging and malfunctions; for the refining engineer, distillation column and equipment plugging and tankage capacity loss, as well as catalyst deactivation; for the transportation engineer, pipeline plugging and capacity loss. (Leontaritis K. J., 1989). Two types of solid deposits will be considered in this study, namely: - Asphaltene, and Wax.

2.4.1 Causes of Solid Deposits

Field experience (de Boer et al, 1995, Kokal and Sayegh 1995) and experimental observations (Fuhr et al, 1991, Fotland 1996, Andersen, 1994, Hammami et al, 1995; Wang et al 1999) indicate that solid deposition is dependent on the following factors: -

- i. Fluid composition

- ii. Pressure
- iii. Temperature
- iv. Flow characteristics
- v. The structure of the conduit (Pipeline) through which the fluid is flowing.

Since this study is on an existing pipeline, it will therefore focus on the effect of fluid composition on solid deposition.

2.4.2 Effects of Solid deposition



Figure 2.2 Section of a Pipeline Showing Effects of Solid Deposition.

As shown in figure 2.2, Solid deposition has the following effects:

- i. Reduction in pipe internal diameter
- ii. Increase/Change in roughness of the pipeline
- iii. Contamination of the fluid
- iv. Increase in pressure loss along the pipeline
- v. Change in composition of the fluid
- vi. Reduction in volume of the fluid transported
- vii. Interference with valve operation and instrumentation, thereby causing operational and safety problems.

2.4.3 Asphaltene Deposition

Available laboratory data indicate that separated asphaltenes from crude oils usually consists of condensed aromatic and naphthenic molecules of molar mass ranging from several hundred to several thousands grams per mole. They also consist of polar molecules containing much of the heteroatom (N, O, S) and metal (Ni and V) content of heavy oils (Hammami et al 1999).

Many researchers define asphaltene as the normal-pentane-insoluble but benzene-soluble fraction of the crude oil (Long, R.B., 1981, Speight, J.G. et al, 1981, Bouszynski, M .M., 1981, McKay et al, 1978). Asphaltenes do not melt on heating but decompose, forming carbon and volatile products above 300°C to 400°C. The wide range of asphaltene-size distribution suggests that they exist in crude oil as both dissolved and suspended particles. They are lyophilic with aromatics. Suspended asphaltenes are dispersed and stabilized primarily by resin molecules present in the crude oil. The degree of dispersion of asphaltenes in crude oils depends on the chemical composition of the crude. With respect to paraffins like pentane, asphaltenes are lyophobic and they coagulate and then precipitate.

Addition of compounds with molecules that differ greatly from resins in terms of size, structure and solubility, shifts the existing equilibrium in the non-asphaltene portion of the crude oil. This causes the resin molecules to desorb from the surface of the asphaltenes in an attempt to re-establish the thermodynamic equilibrium that existed in the crude oil. This desorption of peptizing resins forces the asphaltene micelles to agglomerate in order to reduce their overall surface free energy. If sufficient quantities of the particular solvent are added to the oil, the asphaltene molecules aggregate to such an extent that the particles overcome the Brownian forces of suspension and begin to precipitate (Ferworn, 1995). This shows that the type and/or quantity of solvent added to the crude oil is important to the quantity and characteristics of the asphaltenes precipitated.

The actual chemical structure of Asphaltenes is difficult to define, however, some researchers have attempted to postulate model structures for Asphaltenes, as shown in figures 2.3 and 2.4

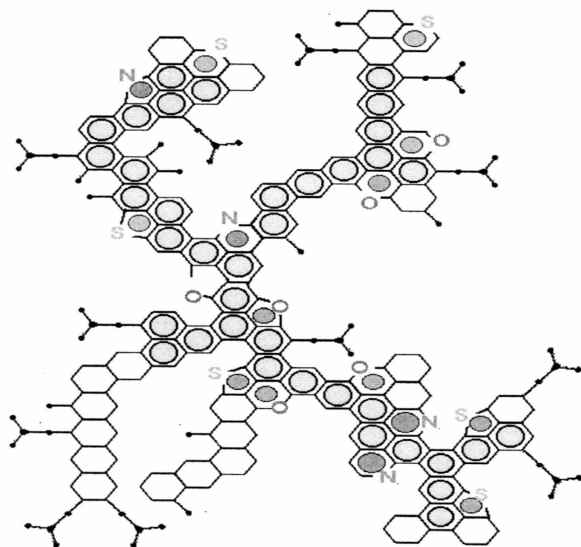


Figure 2.3: Molecular structure of asphaltene by Altamirano, et al (IMP Bulletin 1986)

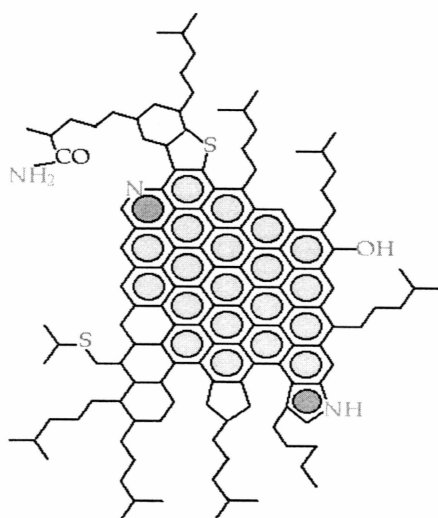


Figure 2.4: Molecular structure of asphaltene postulated by Carbognani (<http://tiger.uic.edu/~mansori/Asphaltene>)

Mechanism of Asphaltene Deposition

Understanding the mechanics of asphaltene flocculation/precipitation and taking care of them will result in more economical, environmental friendly and speedier GTL/Crude oil transportation. There are four known mechanisms of asphaltene deposition.

Polydispersity Effect

Chemical compositions of crude oils determine the degree of asphaltene dispersion in it (Kawanaka et al, 1991). An upset in the polydisperse balance of the polar/non-polar and light/heavy molecules of the crude oil leads to asphaltene flocculation/deposition. An increase in the paraffinic hydrocarbon content of a crude oil, leads to separation of the asphaltene particles into solid aggregates.

Steric Colloidal Effects

Asphaltenes have a strong tendency for self-association (Mansoori, G. A. 1997). Increase in paraffinic hydrocarbon content of a crude oil, causes asphaltenes to form colloids, separate into aggregates and then remain suspended in the crude oil by some peptizing agents like resins, which will be absorbed on their surface and keep them afloat. Stability of such steric colloids is dependent upon the concentration of the peptizing agent, the equilibrium conditions between the peptizing agent in solution and on the surface of the asphaltenes. Concentration of the peptizing agent in the oil determines its amount adsorbed (Mansoori, 1994; Kim et al, 1994; Ray et al, 1957; Katz and Beu, 1945; Witherspoon and Winniford, 1967).

Aggregation Effect

When the concentration of the peptizing agent in the crude oil drops to a point at which its adsorbed amount is not high enough to cover the entire asphaltene

surface, this permits the asphaltene to aggregate, grow in size and flocculate (Mukhametzyanov and Kuzeev, 1991; Kim et al, 1994; park and Mansoori, 1988).

Electro-Kinetic Effect

Motion of charged colloidal particles leads to development of electro-potential difference along the pipeline, which could then cause a change in the charged and colloidal particles farther down the pipeline. This results in untimely deposition and plugging of the pipeline. Factors influencing this effect are the electrical, thermal and wettability characteristics of the pipeline flow regime, temperature, pressure, crude oil properties, and characteristics of the asphaltenes (Lichaa and Herrera, 1975; Mansoori, 1994; Escobedo and Mansoori, 1992).

2.4.4 Wax Deposition

Nature of Waxes

Petroleum wax consists predominantly of normal paraffin hydrocarbons (C15 – C75) known as paraffin wax. Waxes from iso-paraffins and naphthenes are also known. Some waxes have an appreciable quantity of aromatics. Figure 2.5 shows the structural representation of waxes. Waxes are thermo-plastic in nature and depending on their temperature and pressure, hydrocarbon waxes can exist in various states of matter (Solid, Liquid, or Gas). Because wax is plastic in nature, it usually deforms under pressure without application of heat. Crystals are formed when waxes freeze. Crystals from paraffins are known as macrocrystalline wax, while those from naphthenes are known as microcrystalline wax. One important parameter that characterizes the waxing potential of fluids is their cloud point or wax appearance temperature. As long as operating temperatures remain above the cloud point, wax flocculation/deposition will not occur. The following summarizes the general features of wax:

- Combustible
- Insoluble in water

- Solid at ambient temperature
- Liquid at 100 to 200°F
- Thermoplastic in nature

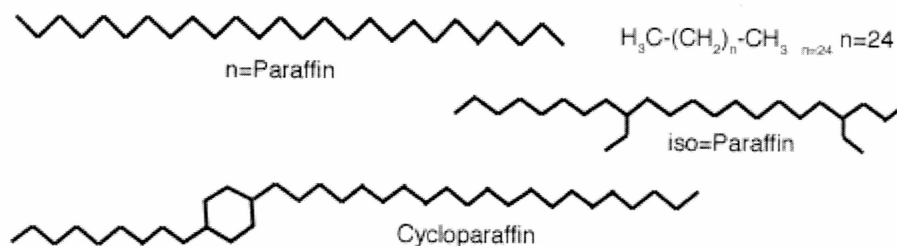


Figure 2.5 Structural representations of waxes

Both n-paraffins and iso-paraffins are flexible hydrocarbon molecules and, hence, tend to cluster together and precipitate from crude oil as solids. Being branched molecules, however, the iso-paraffins tend to delay the formation of wax nuclei and usually form unstable solids. Aromatics are good solvents for paraffinic waxes. Cycloparaffins are stiff and bulky in nature. They tend to disturb and/or disrupt the wax nucleation and growth process. Resins, unlike in the case of Asphaltenes precipitation, do not have a direct effect on wax deposition. The presence of impurities and/or other amorphous solids (such as Asphaltenes) in the oil usually induces wax nucleation process, as they tend to lower the energy barrier for forming the critical wax nucleus (Hamammi and Raines, 1997). It has been reported, however, that the presence of Asphaltene solids which are amorphous in nature act as wax inhibitors (Woo, et al, 1984; Misra, et al, 1995). Whether Asphaltenes induce or inhibit wax formation/deposition depends on their relative concentrations, nature, and sizes.

For temperatures of operational interest, that is, above approximately 0°C, wax consists mainly of C18+ n-paraffins. In practice Wax Appearance Temperature is the most difficult point on the precipitation curve to measure, as it is theoretically the point where the first infinitesimally small amounts of wax is formed. Experimentally,

it is only possible to detect a finite amount of wax and different experimental methods differ in their ability to detect small amounts of wax. Recent survey suggested that uncertainties in Wax Appearance Temperature for good modern measurements may be as $\pm 5^{\circ}\text{F}$. For older measurements the uncertainties can be considerably higher.

Wax deposition is a concern, particularly to a long pipeline in an arctic environment like the Trans Alaska Pipeline System, because this means greater residence time of the oil, 9 days in the case of Trans Alaska Pipeline System (TAPS), in the pipeline. This long residence time permits more heat loss and leads to lower oil temperatures, which in turn can lead to wax precipitation and deposition.

Paraffin Wax Growth Process

As the temperature of the crude oil is lowered towards its wax appearance point, the energy of molecular motion becomes increasingly hindered, and the paraffin molecules in the solution tend to move closer together and form clusters of adjacently aligned chains. The paraffin molecules continue to attach and detach to and from these ordered sites until the clusters reach a critical size and become stable. This process is called nucleation and the clusters are called nuclei. The stability of these nuclei depend on the melting temperature of the wax as they are disrupted by thermal motion above the wax appearance temperature. Once the nuclei are formed and the temperature is kept at or below the wax appearance temperature, additional molecules are laid down successively on the nucleation sites and become part of the growing lamellar structure.

Mechanics of Lateral Transport/Deposition of Waxes

Burger, E. D., (1981) identified three mechanisms contributing to lateral transport and deposition of waxes. These are: - Molecular diffusion, Brownian diffusion, and Shear dispersion.

Molecular Diffusion

For all flow conditions, oil will be in laminar flow either throughout the pipe or at least in a thin laminar sub-layer adjacent to the pipe wall. When the oil is cooling, there exists a temperature gradient across the laminar sublayer. The amount of wax dissolved in solution decreases as the temperature decreases. The temperature profile near the wall, therefore, leads to a concentration gradient of dissolved wax, and this dissolved wax is transported toward the wall by molecular diffusion. When this diffusing material reaches the solid/liquid interface, it drops out of solution (Burger et al, 1981). The rate of transport to the wall is represented by the Fick's diffusion equation

$$\frac{dG}{dt} = D_m A \frac{dC}{dY} \quad 2.12$$

Or in terms of directly measurable quantities

$$W_m = \rho_r A D_m \frac{dC}{dT} \cdot \frac{dT}{dy} \quad 2.13$$

Where:

W_m is the rate of waxy crystal deposition due to molecular diffusion, ρ_r is the wax density, D_m is the molecular diffusion coefficient, A is the deposition area, $\frac{dC}{dT}$ is the solubility coefficient of the wax crystals in the fluid, and $\frac{dT}{dy}$ is the radial temperature gradient at the wall.

Brownian Diffusion

Small waxy crystals, when suspended in the fluid, will be bombarded continually by thermally agitated fluid molecules. These collisions lead to small random Brownian movements of the suspended particles. According to Green H.L. et

al (1957), the Brownian diffusion coefficient for spherical, non-interacting particles is given by: -

$$D_b = \frac{RT_a}{6\pi\mu aN} \quad 2.14$$

Where R is the universal gas constant, T_a is absolute temperature, μ is viscosity, a is particle diameter and N is Avagadro's number.

Shear Dispersion

For low volumetric fractions of precipitated solids, which are of interest for wax deposition problem, the combined data of Eckstein E. C., (1975) and Bailey D.G. (1975), suggest that the shear dispersion coefficient is given approximately by:

$$D_s = \frac{a^2 \gamma C_w^*}{10} \quad 2.15$$

Velocity gradient in the flow causes shear transport of precipitated waxes to the wall. The empirical equation that describes wax deposition rate at the solid/liquid interface (Burger et al, 1981) is given by: -

$$W_{sb} = k^* C_w^* \gamma A \quad 2.16$$

Where K^* is an empirical constant, which must be determined for each particular deposition system, is analogous to rate of reaction constant for a chemical reaction. C_w is the concentration of precipitated waxes at the pipe wall. γ is the shear rate, A is the deposition area, and a is the particle diameter.

From equation 2.16, it is clear that deposition rate increases linearly with shear rate. Other researchers claim that deposition rate increases with increasing shear

rate while the flow is laminar, but then decreases with increasing shear rate as the flow becomes turbulent (Weigarten et al, 1988). Wax deposit due to shear transport increases linearly with shear rate until the shear stress at the edge of the deposit reaches the shear strength of the deposited wax. At shear rates higher than this critical value, the waxes shear off as soon as they are deposited, and the rate of total deposition approaches zero. The onset of sloughing is not related to a transition from laminar to turbulent flow (Weinngarten et al, 1998).

2.4.5 Solid Deposit Prevention and Remediation

Solid deposition can be controlled through better understanding of the mechanics that cause the deposition in the first place. Process can be altered to minimize the deposition. Prevention and Remediation is dependent on the type of solid (Asphaltene or Wax)

Prevention and Remediation of Asphaltene Deposition

Two general methods can be used to prevent and/or manage Asphaltene deposition in Trans Alaska Pipeline System. These are: - 1) Mechanical method, 2) Chemical method.

Mechanical method.

This can be used to remove Asphaltene deposits from pipelines; however, Asphaltenes are more brittle and harder to remove than typical wax deposits. The following tools can be used: a) Pigs, b) wireline tools, c) coiled tubing.

Effective removal requires that the appropriate type of pig be used and that pigging be performed on a regular basis. The pigs should be designed specifically for solid removal. Therefore disk or cup pig should be used since they impart much more force on the pipe wall. Spheres or foam pigs are not adequate for Asphaltene removal.

In addition, a bypass pig (one that permits part of the fluid stream to pass through it) allows the removed Asphaltenes to disperse into the crude oil ahead of the pig. This therefore prevents solid buildup in front of the pig and decreases the likelihood of the pig getting stuck.

Wireline cutting is an effective means of removing Asphaltene from the pipeline provided that the required frequency is not excessive. Coiled Tubing also can be used to remove Asphaltene deposits from the pipeline.

Chemical Methods

Chemical treatment techniques include: Addition of aromatic solvents, antifoulants, and dispersants. Asphaltenes are very soluble in aromatic solvents such as benzene and xylene even at very low temperatures. Antifoulants and dispersants are developed to combat against the onset of Asphaltene flocculation. Some of these chemicals in effect supply “extra” resins to stabilize the Asphaltene molecules. They surround the Asphaltene molecules in a manner similar to the natural resin material.

Prevention and Management of Wax Deposition

Wax deposits in Trans Alaska Pipeline systems can be prevented and managed by any of the following four methods:

1. Mechanical method
2. Thermal method
3. Chemical method
4. Biotechnology method
5. Magnetic method

Mechanical method

This is the method of running a scraper, which mechanically cuts the wax deposit from the pipeline. Wirelines, pigs, and calipers are examples. They are sent

down the line, carried along by the flow of crude, and mechanically scrape off the wax and redisperses it in the bulk oil in front of the pig.

Thermal method

Addition of heat by such methods as induction heating will guarantee that the fluid being transported will stay above its wax appearance temperature. Installing line heaters, and circulation of hot oil are ways that can be used to melt or increase the solubility of wax deposits.

Chemical method

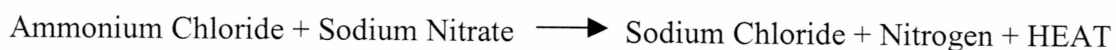
Wax deposition in Trans Alaska Pipeline can be controlled chemically by the use of one or all of the following: wax inhibitors, solvent washers, pour point depressants, and heat inducers.

Wax inhibitors co-crystallize with the wax to prevent wax crystal structures from forming on the pipe wall. Often dispersants and surfactants are added. The dispersants coat wax crystals to keep them from agglomerating and surfactants act to water wet the wax crystals so as to prevent their adherence to each other or to the pipe wall.

Solvent washers like xylene can be circulated through the pipeline to remove wax deposits. They are more effective than the hot oil treatments and cause less damage, but are considerably more expensive.

Pour point depressants or wax crystal modifiers can be used at ppm concentration levels to modify the wax crystal structure. They significantly reduce the pour point, viscosity, and yield stress, but these chemicals may not reduce rates of wax build up on pipe walls.

Heat Inducer is a process in which two salt solutions that have a strong exothermic reaction are mixed together to liberate heat.



This reaction is performed ideally at the point in a pipeline where wax deposits exit. The practical application of this process is of course quite difficult in a very long pipeline like the Trans Alaska Pipeline System.

Biotechnology method

It has been reported that microbial degradation has a beneficial effect on waxy crude oils and their effectiveness is most likely due to biosurfactancy. This process therefore, can be used to prevent wax depositions.

Magnetic method

Strong magnetic fields have been employed with success, in certain cases, to control wax deposition. The theoretical basis for such an approach suggests that forming waxes, when subjected to an intense magnetic field, will be displaced from their preferred crystal alignment. This disalignment then either prevents or interferes with the crystal's continued networking.

2.5 Reid Vapor Pressure

Part of this study is to experimentally determine the reid vapor pressure of GTL and GTL/Crude oil blends. Vapor pressure of a liquid is a function of both temperature and composition, if either is changed from some reference point, then the vapor pressure will change (Reed, D.B et al, 1990). It is the lowest absolute pressure of a liquid at a given temperature at which the liquid remains liquid. Reid vapor pressure is a measurement of the stabilized pressure exerted by a volume of liquid at 100°F. Numerically the relationship between true vapor pressure (TVP) and reid vapor pressure (RVP) is expressed by the following equations: -

$$TVP = (RVP) \exp^{C_o (IRTEMP - ITEMP)} \quad 2.17$$

Where c_o = constant dependent upon the value of RVP

$$ITEMP = \frac{1}{555.69^\circ R}$$

$$IRTEMP = \frac{1}{(T_s + 459.69^\circ R)} \quad 2.18$$

T_s = temperature of the stored fluid

The value of the constant term C_o depends on the given value of RVP. Values of C_o for different RVP numbers are given in table 2.1.

However, an error was discovered in the API nomograph calculated values of TVP so that the RVP was not equal to TVP at 100°F as was expected given the general definition of RVP. In order to obtain reasonable TVP numbers, correction factors (C_F) were developed and should be added to the calculation values of TVP. Therefore:

Corrected TVP = Calculated TVP + C_F

The correction factor is dependent on RVP by the following equations: -

If RVP is less than 3

$$C_F = (0.04) \times (RVP) + 0.1 \quad 2.19$$

If RVP is greater than 3

$$C_F = \exp^{[(2.3452061 \log(RVP)) - 4.132622]} \quad 2.20$$

Table 2.1 Values of C_o for RVP Numbers (www.arb.ca.gov/DRDB/SB/CURHTML)

RVP	C_o
$0 < \text{RVP} < 2$	-6622.5
$2 < \text{RVP} < 3$	-6439.2
$\text{RVP} = 3$	-6255.9
$3 < \text{RVP} < 4$	-6212.1
$4 = \text{RVP}$	-6169.2
$4 < \text{RVP} < 5$	-6177.9
$\text{RVP} = 5$	-6186.5
$5 < \text{RVP} < 6$	-6220.4
$\text{RVP} = 6$	-6254.3
$6 < \text{RVP} < 7$	-6182.1
$\text{RVP} = 7$	-6109.8
$7 < \text{RVP} < 8$	-6238.9
$\text{RVP} = 8$	-6367.9
$8 < \text{RVP} < 9$	-6477.5
$\text{RVP} = 9$	-6587.9
$9 < \text{RVP} < 10$	-6910.5
$\text{RVP} = 10$	-7234.0
$10 < \text{RVP} 15$	-8178.0

2.5.1 Effect of Vapor Pressure on Fluid Transportation

Vapor pressure is a thermodynamic property of the liquid, which in conjunction with other thermodynamic properties determines the emission rate and volatility of the liquid. The consistency of a liquid volume and composition is a function of its vapor pressure.

Solid deposition is to some extent dependent on the vapor pressure of the liquid. More solids tend to precipitate when liquid is below its vapor pressure as a result of change in the liquid volume and composition.

The limiting factor in pumping liquids with a jet pump is the vapor pressure of the liquid involved so as to avoid potential vapor locking of pumps due to cavitation.

Pump Cavitation

Pump cavitation is the dynamic process of gas cavity growth and implosion in a pump. It occurs when there is inadequate Net Positive Suction Head Available (NPSHA), that is, when the total energy in the fluid, expressed as equivalent pressure, is equal to or less than the vapor pressure of the fluid. It is a phenomenon that takes place when a fluid in liquid phase vaporizes as it passes through a pump and then quickly turns back into a liquid. The bubbles form at the position of lowest pressure at the pump inlet, which is just prior to the fluid being acted upon by the impeller vanes. Once the vapor pockets enter the impeller, the process begins to reverse itself. As the vapor reaches the discharge side of the pump, it is subjected to a high positive pressure, which condenses the vapor back to liquid. The collapse of the vapor bubbles creates destructive micro jets of liquid strong enough to damage the pump. The compression of the vapor bubbles produces a small shock wave that impacts the impeller surface and pits away at the metal creating over time large eroded areas and subsequent failure.

Effects of cavitation

1. Reduction in Pump Capacity

The formation of bubbles decreases the space available for the liquid and thus diminishes pumping capacity. If the bubbles are big enough for the impeller, the pump “chokes”, that is, the pump loses all suction resulting in a total reduction in flow. The unequal and uneven formation and collapse of bubbles causes fluctuations in the flow and the pumping of liquid occurs in spurts (Sahdev, 2003).

2. Reduction in the Energy Head

Unlike liquid, bubbles are compressible. The head developed diminishes drastically because of the use of energy to increase the velocity of the liquid used to fill up the cavities, as the bubbles collapse.

3. Abnormal Sound and Vibrations

The movement of bubbles with very high velocities from low-pressure area to a high-pressure area and the subsequent collapse creates shockwaves producing abnormal sounds and vibrations.

4. Erosion or Pitting of Pump Parts

Collapse of bubbles during cavitation takes place at a sonic speed ejecting destructive micro jets of extremely high velocity (as high as 1000 m/s) liquid strong enough to cause extreme erosion of the pump parts, particularly the impellers.

5. Mechanical Deformation

Longer duration of cavitation condition results in unbalancing (as a result of unequal distribution in bubble formation and collapse) of radial and axial

thrusts on the impeller. This unbalancing leads to the following mechanical problems:

- a. Bending and deflection of shafts
 - b. Bearing damage and rubs from radial vibration
 - c. Damage of thrust bearing
 - d. Breaking of impeller check-nuts
 - e. Damage of seals
6. Corrosion
- The collapse of bubbles destroys existing protective layers making the metal surface vulnerable to chemical attack (corrosion). Thus, even slight cavitation may lead to considerable damage to the materials.

CHAPTER 3

PIPELINE SPECIFICATION AND TEST FLUID PROPERTIES

3.1 Pipe Specifications

The Trans Alaska Pipeline System (TAPS) is 800.32 miles long with outer diameter of 48 inches. The pipeline thickness is 0.462 inches for 466 miles and 0.562 inches for 334 miles. It starts at Prudhoe Bay and ends at Valdez terminal with a total line fill of 9059057 barrels. Its maximum design pressure is 1180Psi and its maximum operating pressure is 1180Psi. The original design of the pipeline has 12 pump stations with 4 pumps each. Pump station 5 is a relief station with no pumping capacity, it only reinjects oil drained down for pressure relief, but does not have mainline pumps and does not boast total stream. Pump stations 2,6,8, and 10 are currently on standby mode. Control system of the pipeline provides instantaneous monitoring and control of all significant aspects of operation and pipeline leak detection. The locations of the various pump stations with their elevations are shown in table 3.1, while figure 3.1 is the map of Alaska showing the Trans Alaska Pipeline System and the pump stations. Trans Alaska pipeline maximum daily throughput is 2.136 million barrels, with 11 pump stations operating. Rates exceed 1440,000 bbl/day with drag reduction agent (DRA) injection. The pipeline is based primarily on the soil conditions encountered. There are four design modes namely: -

- i. Above-ground mode
- ii. Conventional below-ground mode
- iii. Special burial, non-refrigerated
- iv. Special burial, refrigerated

Table 3.1 Locations and Elevation of Pump Stations (TAPS FACTS, 1998)

Pump Station	Location	Distance		Elevation	
		Miles	Km	Feet	Meters
1	Prudhoe Bay	0	0	39	11.89
2	Happy Valley	57.76	92.93	602	184.48
3	Happy Valley	104.27	167.77	1383	421.54
4	Galbraith Lake	144.05	231.78	2763	842.16
5	Prospect Creek	274.74	442.06	1066	324.92
6	Five Mile	354.94	571.10	881	268.53
7	Fairbanks	414.12	666.32	905	275.84
8	Eielson AFB	489.22	787.15	1029	313.64
9	Big Delta	548.69	882.82	1509	459.94
10	Gulkana	585.77	942.5	2392	729.08
12	Gulkana	735.04	1182.68	1821	555.04
Terminal	Valdez	800.27	1287.63	142	43.28

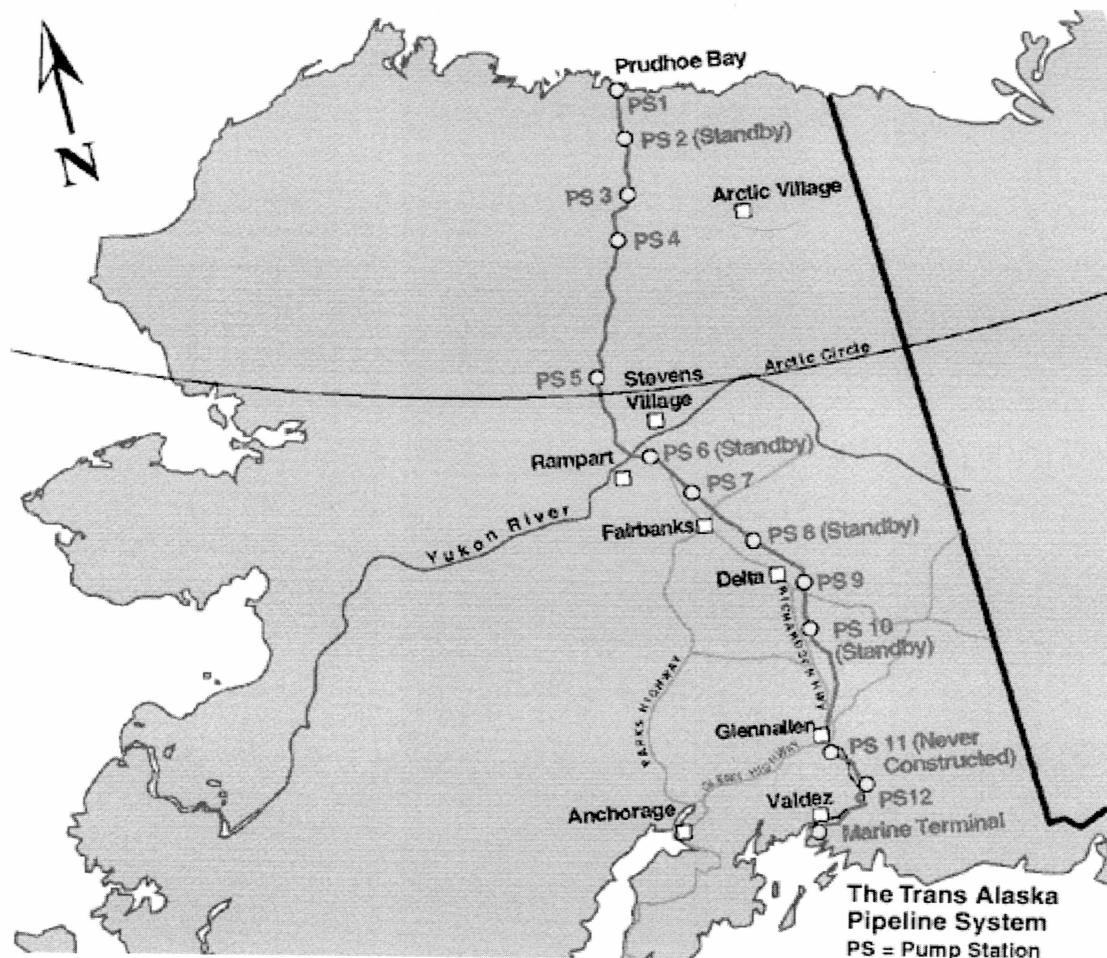


Figure 3.1 Map of Alaska showing the trans Alaska Pipeline and the pump stations (Nerella, 2002)

Above-ground Mode

In areas where heat might cause thawing, specially designed vertical supports were placed into the ground. The supports contain two each, 2-inch pipes called “heat pipes” containing anhydrous ammonia, which vaporizes below ground, rises and condenses above-ground, removing ground heat. Heat is transferred atop the pipes through the walls of the heat pipes to aluminum radiators. Figure 3.2 shows above ground section of the Trans Alaska Pipeline System.

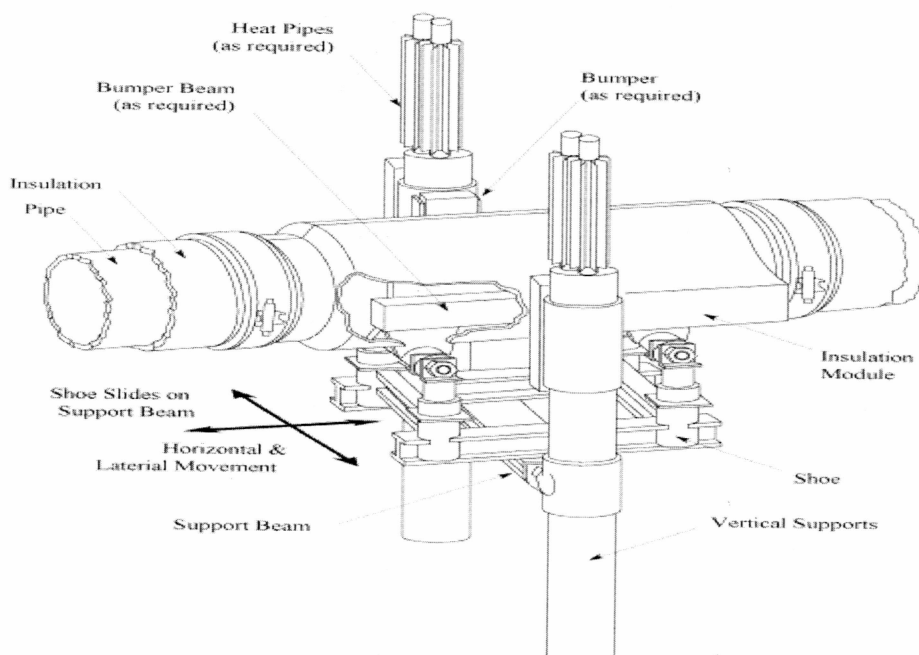


Figure 3.2 Section of the Trans Alaska Pipeline System (Pipeline Facts)

Conventional Below-ground

When either unfrozen or thaw-stable permafrost were encountered, the pipeline was buried in the conventional manner with no special provisions for permafrost.

Special Burial, Non-refrigerated

Where thaw-unstable soils calling for elevated pipeline were encountered, but the pipeline had to be buried for highway, animal crossing, or avoidance of rockslides and avalanches, the line was insulated and buried.

Special Burial, Refrigerated

In some areas the line was insulated and buried in a refrigerated ditch as shown in figure 3.3. The refrigeration circulates chilled brine through loops of 6-inch diameter pipe to keep the soil in a stable frozen condition.

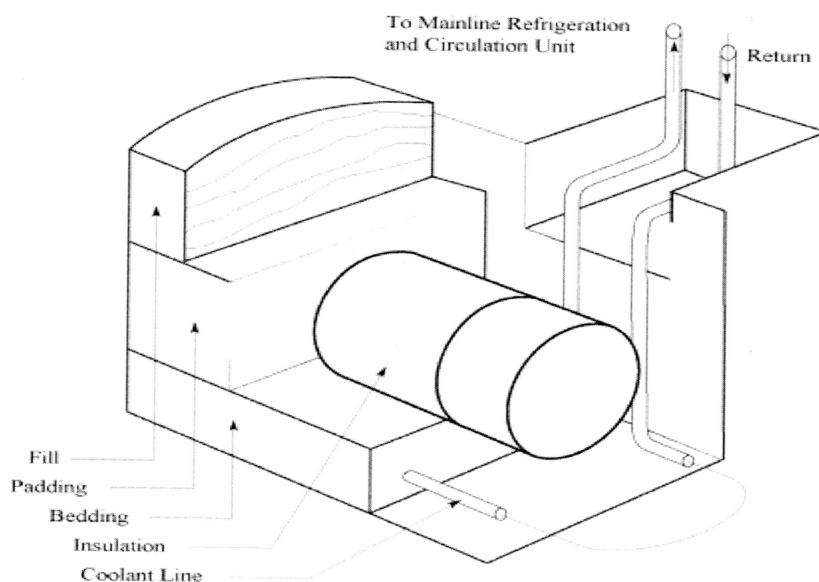


Figure 3.3 Refrigerated-Burial of Pipeline (Pipeline facts)

The insulation thickness is based on the design mode. Elevated pipeline has insulation thickness of 3.75-inches; Refrigerated belowground insulation thickness is 3.2 inches, while conventional belowground is 2-inches to 4-inches.

Thermal Expansion

Every 40 feet length of pipe expands 0.31 inches with each 10°F rise in temperature. Longitudinal expansion of typical 720 feet straight aboveground segment from minimum tie-in temperature to maximum operating temperature is 9 inches. The pipeline does not expand lengthwise but shifts laterally on the aboveground supports due to pipeline anchoring.

Travel Time

The fluid velocity is 3.7 miles per hour and the total time from pump station one to Valdez is 9 days. The travel time for each pipe section is shown in table 3.2.

Table 3.2 Travel Miles, and Line Fill Between Stations (Pipeline Facts, 2003)

From	Hours	Miles	Linefill (bbl)
1-2	15.71	57.76	653,862
2-3	12.65	46.51	526,508
3-4	10.82	39.78	450,322
4-5	35.56	130.77	1,480,358
5-6	21.81	80.18	907,663
6-7	16.09	59.18	669,937
7-8	20.42	75.10	850,156
8-9	16.17	59.46	673,106
9-10	10.09	37.09	419,871
10-11	27.24	100.16	1,133,843
11-12	13.36	49.11	555,941
12-Valdez	17.74	65.22	738,311

Pipeline Temperature

The inlet and exit temperature of the crude oil at working pump stations are shown in table 3.3 (Nerella, 2002)

Table 3.3 Crude oil Temperatures at Various Pump Stations

Pump Station	Inlet Temperature	Exit Temperature
1		115.7
3	83.8	86.4
4	81.3	84.1
5	71.4	Relief Station
7	66.5	70.3
9	72	74.9
12	64.4	64.7
Valdez	64.7	

The above temperatures are for a flow rate of 1.1 mbpd for the month of April. The exit temperature at each pump station is higher than the inlet temperature; this rise is due to the pumps. The abrupt increase in the temperature of the fluid is due to North Pole refinery influence on the volume taken off and injected back at different temperature, which is called North Pole metering.

3.2 Test Fluid Properties

Gas-To-Liquid

Gas-to-Liquid sample used in this study consists primarily of normal paraffins and iso-paraffins, with some alcohols and olefins. This GTL from Laporte is a direct product of Fischer Tropsch process. The final boiling points of samples are altered through distillation to simulate different possible grades of GTL expected in North Slope Alaska.

Three final boiling points were distilled at atmospheric pressure. Figure 3.4 shows the result of the compositional analysis of the GTL samples, carried out at

University of Alaska Fairbanks, using Gas Chromatography Mass Spectrometer (GCMS). The results confirm that the sample consists primarily of normal paraffins, olefins, and alcohols, figure 3.4, (Timmcke, 2002).

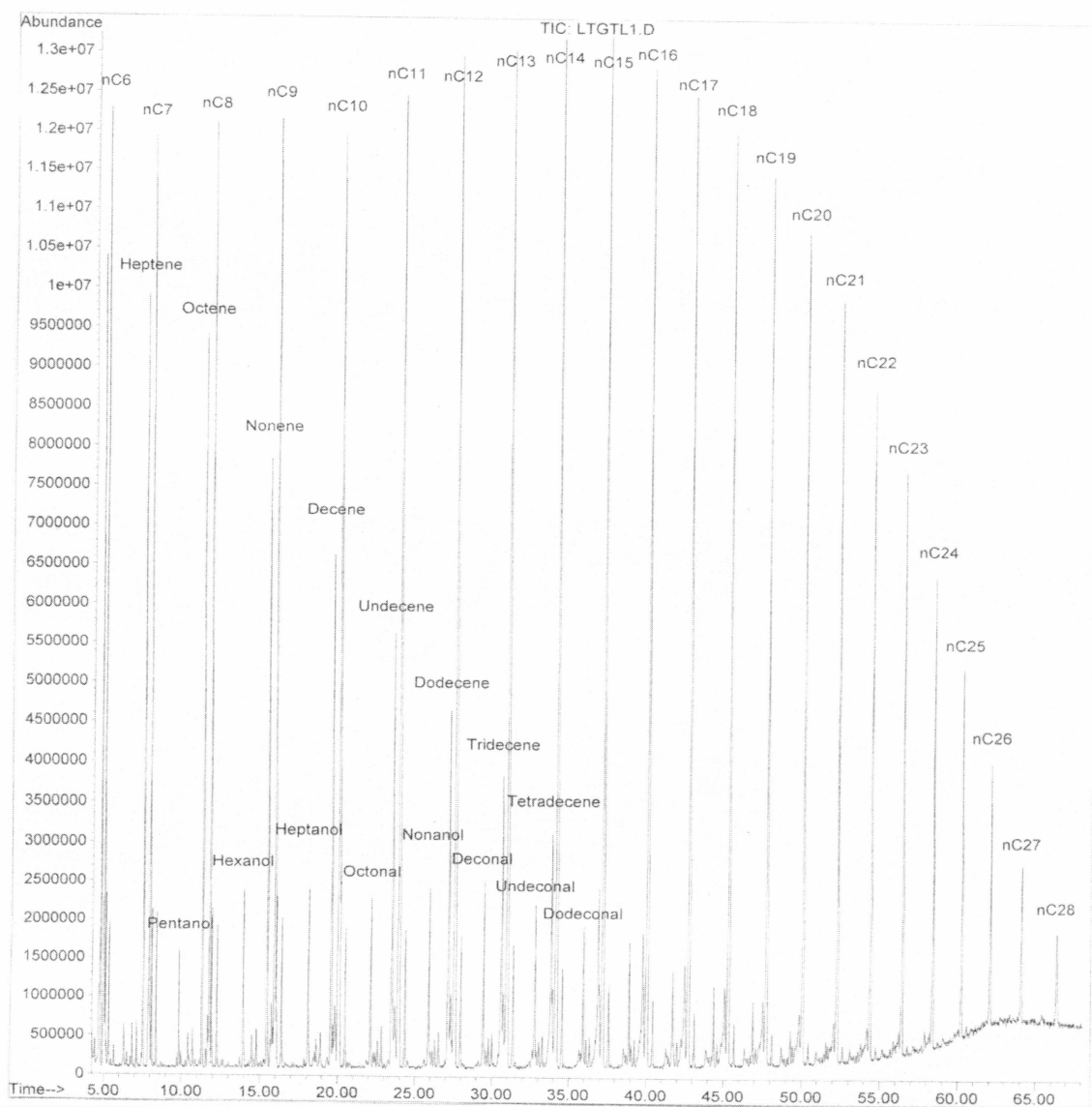


Figure 3.4 Total Ion Chromatograph of Laporte Light GTL (Timmcke, 2002)

Compositional analysis of the light GTL distillations yielded a weight percent carbon number distribution presented in table 3.4. On the average the samples contain 67-weight percent normal paraffin, 28 weight percent olefins, and 5 weight percent alcohols. The graphic representation of the three GTL distillation cut's weight percent carbon distribution is shown in figure 3.5. The compositional distribution shifts towards left with lower boiling point, confirming the reduction in higher molecular weight hydrocarbons that contribute to higher wax appearance points.

Table 3.4 GTL Weight Percent Carbon Number Distribution (Timmcke, 2002)

Carbon Number	Weight Percent		
	254 GTL	302 GTL	344 GTL
< or = 5	3.94	3.38	3.15
6	7.5	7.02	6.16
7	8.28	7.28	6.5
8	9.74	7.85	7.15
9	11.41	8.68	7.85
10	11.47	8.98	8.44
11	11.76	9.04	8.49
12	10.15	8.66	7.77
13	7.97	8.03	7.47
14	6.18	7.20	6.77
15	4.00	6.15	5.93
16	2.87	5.18	5.21
17	2.00	3.77	4.22
18	1.34	2.76	3.45
19	0.86	2.22	2.92
20	0.54	1.45	2.25
21	0.00	1.01	1.84
22	0.00	0.67	1.45
23	0.00	0.42	1.09
24	0.00	0.25	0.73
25	0.00	0.00	0.49
26	0.00	0.00	0.45
27	0.00	0.00	0.22
28	0.00	0.00	0.00
> or = 29	0.00	0.00	0.00

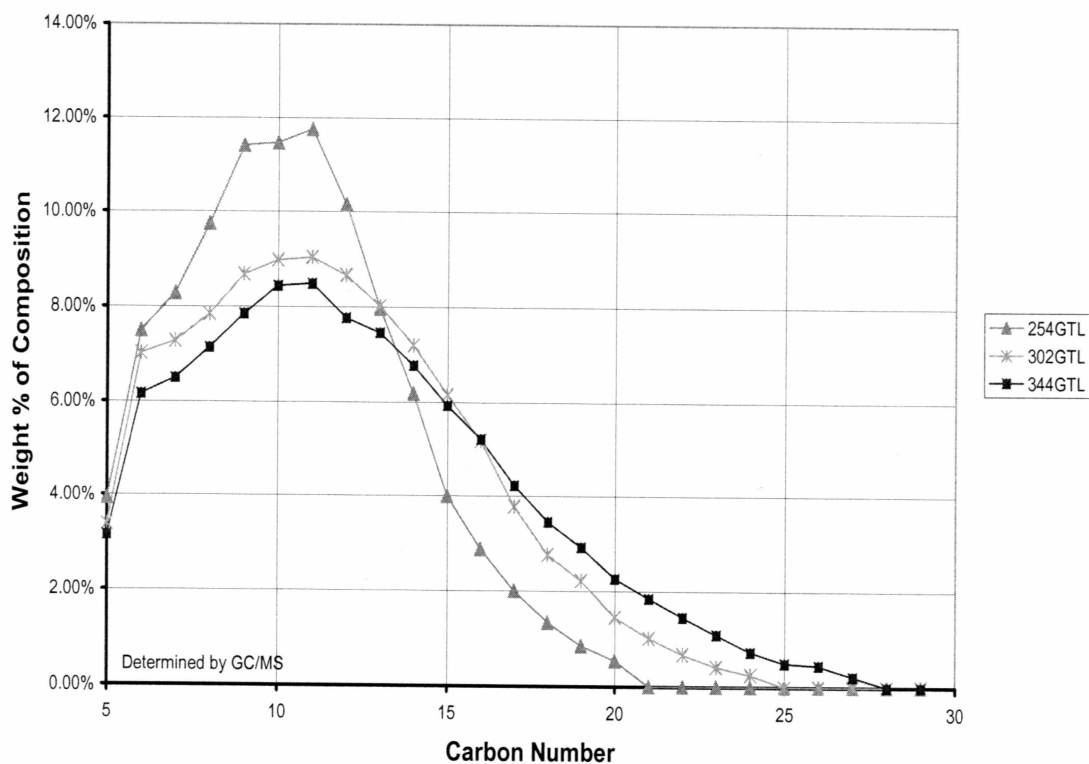


Figure 3.5 GTL Distillate Cut Carbon Number Distribution (Timmcke, 2002)

Another sample used in this study is the F-T Diesel sample provided by DOE. It is a refined product consisting only narrow range of paraffinic hydrocarbons (C12 to C22).

Crude Oil

The crude oil used in this study is Alaska North Slope (ANS) crude supplied by Alyeska Pipeline Service Company. The crude specific gravity at 70°F is 0.862 or 33°API and its viscosity at the same temperature is 17.3 cp.

Blends

GTL and crude oil sample blends are prepared gravimetrically and their proportions are as shown in table 3.5: -

Table 3.5 Percentage of GTL Cuts in the Samples Used

Sample	Percentage (in Crude oil)
F-T Diesel	20
	25
254 Cut*	100
	25
	50
302*	100
	25
	50
344*	100
	25
	50

* 254,302 and 344 cuts stands for the final boiling point temperature of the GTL at atmospheric pressure.

CHAPTER 4

SAMPLE PREPARATION

4.1 Gas-To-Liquid Distillation

Various cuts of GTL are obtained at atmospheric pressure using Herzog Automatic Distillation Analyzer, HDA 627. The Analyzer automatically controls the distillation of samples based on user-selected program. It determines the atmospheric boiling curve, (that is, the vapor temperature in relation to distilled percent volume) of petroleum products.

This analyzer (figure 4.1) consists of a distillation oven with an automatic fire extinguisher, a tempering system for the condenser tube and receiver, an alphanumeric display to show the distillation state with temperature, volume, and a multiple processor system. The computer connected to the instrument is programmed with the test parameters and upon the end of the test run, data are sent back to the computer and saved in the program database. Upon request, the computer prints a comprehensive report. The operator can also compare new data with existing data and save the results in a permanent file. For detailed distillation procedure see Timmcke, 2002.

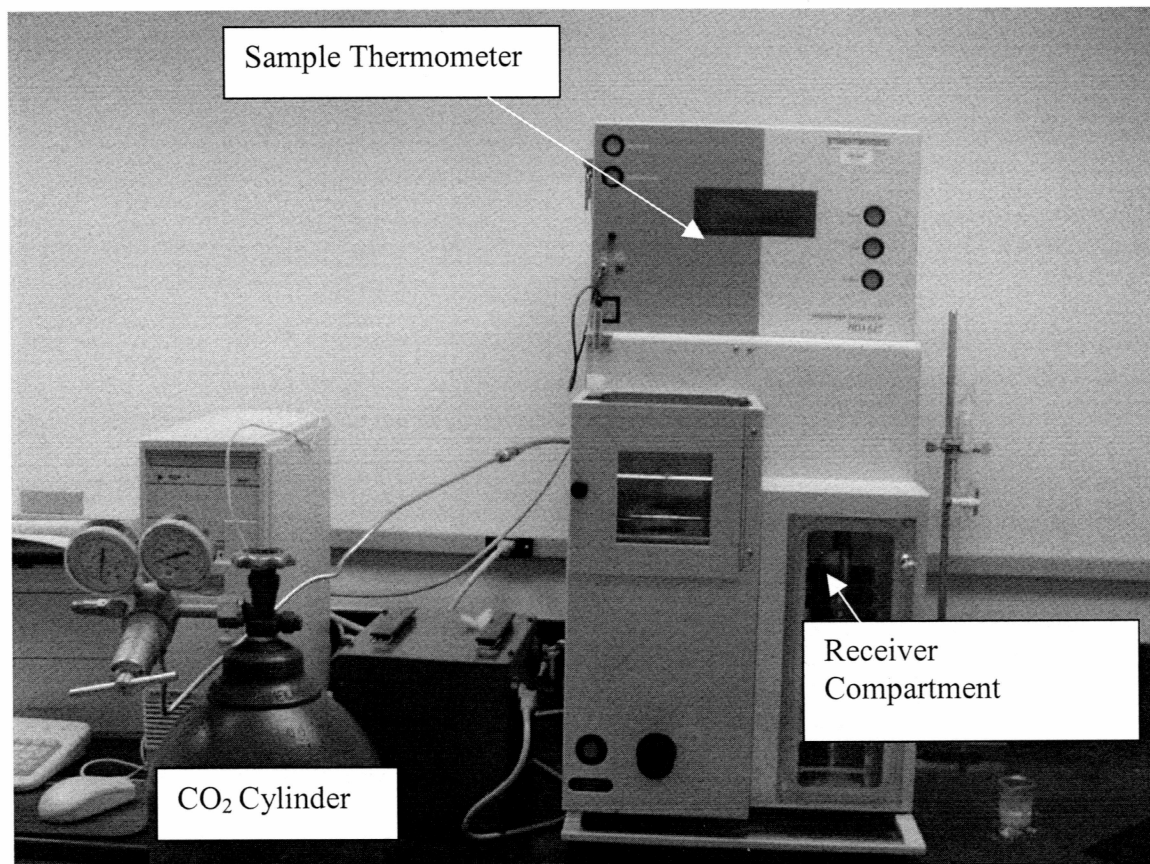


Figure 4.1 Herzog HDA 627 Automatic Distillation Analyzer

4.2 Crude Oil Sampling, Reconditioning and Aliquoting

Alyeska Pipeline Service Company (APSC) supplied all the crude oil samples used in this study. The samples were taken at pipeline conditions and preserved in constant pressure welker cylinders. Before aliquoting the samples, it is necessary to recondition the samples back to the original pipeline conditions. This is done to ensure that the pipeline compositions of the samples are retained.

Description of the Welker Cylinder

Welker cylinder (figure 4.2) is a constant pressure sample cylinder designed to provide a sample receiver capable of retaining the product at pipeline pressures, provide adequate mixers, laboratory repeatability, and safety in handling a sample. The cylinder has two ends internally separated by a floating piston. One end is the product inlet or sampling end, while the other is the precharge end.

At both end of the cylinder is a pressure gauge to read the pressure. An indicator rod is mounted on top of the precharge end. Quick connects and disconnects are used at both the precharge end and sampling end to allow easy Aliquoting of samples without any leak. The mixing rod is used to homogenize the sample while reconditioning.

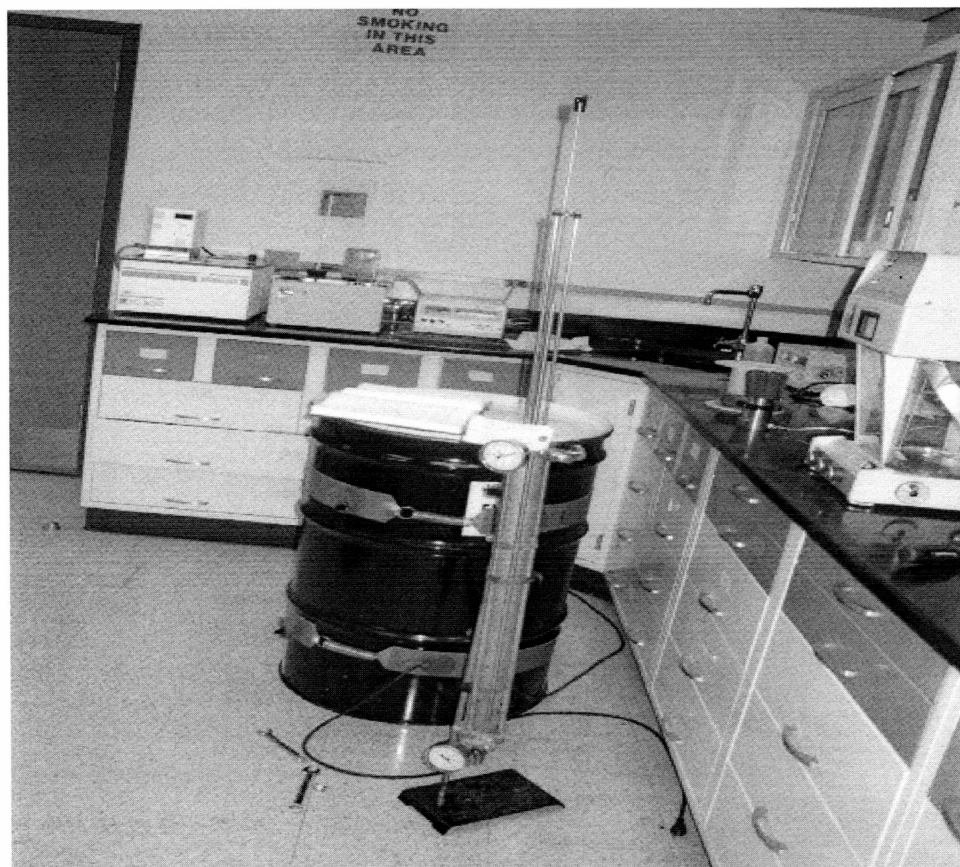


Figure 4.2 Welker Cylinder and 55 gal Drum with Industrial Belt Heaters

Detailed procedure for crude oil Reconditioning and Aliquoting is as outlined by Ramakrishnan, 2000.

4.3 Density Measurement

All the sample blends used in this study were blended gravimetrically, and for accurate blending, density of each cut, and crude oil is required. The instrument used in this measurement is Anton Paar's Digital density meter, DMA 45, figure 4.3.

Materials Used

1. Anton Paar's Digital density Meter DMA-45. This is a digital analyzer consisting of a U-shaped, oscillating sample tube and a system for electronic excitation, frequency counting, and display.
2. Circulating Constant-Temperature Bath. Maintains circulating liquid temperature constant to $\pm 0.1^{\circ}\text{C}$ of the set temperature.
3. Refrigerated Circulating bath. Filled with water and connected to the spare heat exchanger coil submerged in the constant-temperature bath. This is set to provide a continuous circulation of cold water at a set temperature, to the constant-temperature bath.
4. Syringes. Plastic syringes of 2cc or more in volume, with a tip or an adapter tip that will fit the opening of the oscillating tube.
5. Thermometer with holder. Calibrated mercury thermometer graduated to 0.1°C and attached to the thermostat for observing the test temperature.
6. Water. De-ionized water as a calibration standard
7. Toluene, and Acetone, for cleaning the sample tube.

Description of the Density Meter

The meter consists of a glass oscillator inserted into a glass housing consisting of two coaxial tubes. The electric part of the meter excites the oscillator, and a built-in quartz clock measures the period of oscillation approximately every 2 seconds. The

measured period is transmitted to the built in processor. The processor calculates density after each measurement and displays the result in g/cm^3 on the numerical display while the next measurement is taking place. There are two injection ports to the right side of the meter. The upper inlet port is used for flushing out samples and drying the U-tube. The lower port is the sample inlet port. The in-built pump, when switched on, passes air through the upper inlet port. The meter also has a buffer where the values of the calibration constants A and B are stored. The display selector is used to select values of A, B, T and density values.

For any reason the oscillator did not oscillate within the allowed frequency interval (example, immediately after power on or during filling), then the meter performs a display check by displaying 88.8888. If a negative density is calculated due to nonsensical calibration constants, then this also leads to a display check.



Figure 4.3 Anton-Paar Digital Density Meter

A circulation bath with a minimum flow rate of 6-l/min and precision better than $\pm 0.05^{\circ}\text{C}$ is connected to the hose fitting on the back panel of the meter. This brings the measuring cell up to the required temperature. On the spare heat exchanger coil submerged in the constant-temperature bath, is connected the water filled refrigerated circulating bath. Figure 4.4 shows the Density Meter setup at UAF. For detailed Density Meter Calibration and Density Measurement Procedure, see Ramakrishnan, 2000.

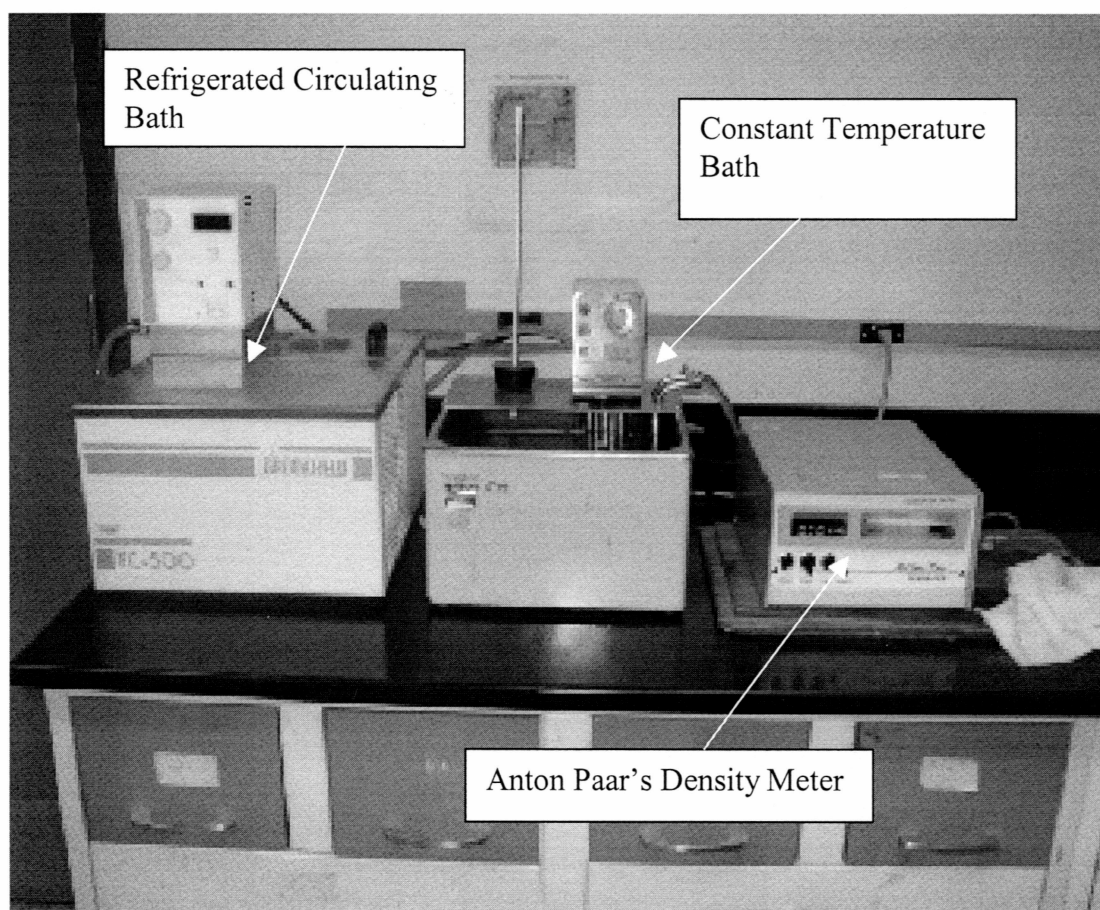


Figure 4.4 Density Meter Setup at University of Alaska Fairbanks

4.4 Blending of Samples

All blends were done gravimetrically. The volume of samples used in this study ranges from 5ml to 500ml.

Blending Procedure

1. Determine the required quantity of sample needed to perform the desired test.
2. Based on the density of the sample components and the volume of the blend required determine the mass of each component necessary to provide the required volume of the component in the blend, at the given mass ratio.

Using

$$V = \frac{\alpha M}{\rho_G} + \frac{(1-\alpha)M}{\rho_C} \quad 4.5$$

Therefore

$$M = \frac{\rho_G \rho_C V}{\rho_C \alpha + (1-\alpha) \rho_G} \quad 4.6$$

Where

α is the mass fraction of GTL in the blend

M is the total mass of the blend that will give the required volume.

With M calculated, the blend can be made using either Mass balance or Pipette

Using Mass balance:

$$\text{Mass of GTL} = \alpha M \quad 4.7$$

$$\text{Mass of Crude} = (1-\alpha)M \quad 4.8$$

Using Pipette:

$$\text{Volume of GTL} = \frac{\alpha M}{\rho_G} \quad 4.9$$

$$\text{Volume of Crude} = \frac{(1-\alpha)M}{\rho_C} \quad 4.10$$

Example Calculation:

To blend 500ml of 3:1 Crude oil/302 GTL sample, the following steps are taken:

- i. Determine the density of each of the components

$$\text{Density of 302 at } 21^{\circ}\text{C} = 0.724$$

$$\text{Density of crude oil at } 21^{\circ}\text{C} = 0.862$$

- ii. Determine the mass of the blend that will give 500ml

$$M = \frac{0.724 \times 0.862 \times 500}{(0.862 \times 0.25) + (0.724 \times 0.75)} = 411.4$$

$$\text{Mass of 302 GTL} = 0.25 \times 411.4 = 102.8$$

$$\text{Mass of Crude} = 0.75 \times 411.4 = 308.6$$

- iii. Determine the volume of each component (if using pipette)

$$\text{Volume of 302 GTL} = \frac{0.25 \times 411.4}{0.724} = 142.1 \text{ ml}$$

$$\text{Volume of Crude Oil} = \frac{0.75 \times 411.4}{0.862} = 357.9 \text{ ml}$$

CHAPTER 5

EXPERIMENTAL SETUP AND PROCEDURE

Basically, four major experiments were carried out in this study. Table 5.1 summarizes the objective of, and standard/method as well as equipment used in each experiment.

Table 5.1 Overview of Experiments, Objectives, Standards, and Equipments used in this Study.

Experiment	Objective	Standard/Method	Equipment
Static Asphaltene Deposition Test	To determine the amount of Asphaltene in ANS crude	Petroleum Resource Research Center (PRRC) 02-02	ZapCap-S Sterile Bottle-Top Filters, S&S, Vacuum Source, Mettler AE160 Mass Balance
Wax Appearance Point	To determine the wax appearance temperature of samples	1) ASTM D3117 2) Viscometric	Koehler K29760 Brookfield Viscometer
Flocculation Onset Titration	1) To determine whether or not GTL is an Asphaltene flocculant 2) To check the stability of ANS crude to Asphaltene deposition	Viscometric Viscometric	Brookfield Viscometer Cannon-Fenske Viscometer
Reid Vapor Pressure	To determine the vapor pressure of GTL and GTL/Crude oil blends	ASTM D 323	Herzog Semiautomatic Analyzer

5.1 Static Asphaltene Deposition Test (PRRC 02-02 with some modifications)

This follows ASTM recommended procedure for separating Asphaltenes from crude oil (ASTM D2007-80) with some modifications. ASTM standard specifies adding a volume of n-pentane that is 40 times the volume of the crude oil. The main modification is to use either n-heptane or GTL instead of n-Pentane as the standard precipitant. The objective of this test is to: -

- a) Determine the amount of Asphaltene in ANS crude
- b) Whether or not GTL is a precipitant of Asphaltene

5.1.1 Materials Used

- a) ZapCap-S Sterile Bottle-Top Filters,



Figure 5.1 ZapCap-S Sterile Bottle-Top Filters

This is a disposable 500ml device (Figure 5.1) designed for vacuum filtration of samples. The 76mm (3") diameter membrane is pure cellulose acetate. The filter pore size is 0.22 μ m.

- b) Vacuum Source

- c) Mettler AE160 Mass Balance
- d) 1000ml glass flask

5.1.2 Procedure for Separating Asphaltenes from Crude Oils

1. Accurately measure 20ml of oil into a glass flask.
2. Add 800ml of GTL (or other asphaltene precipitant, as needed) to the flask. Seal the flask with a stopper and shake the mixture thoroughly.
3. Age the mixture for two days at ambient conditions. Shake the flask at least twice during this period.
4. Pre-weigh the ZapCap-S Sterile Bottle-Top filter.
5. Pour about 450ml of the oil/precipitant mixture into the bottle-top filter and cover the top to reduce evaporation during filtration.
6. Connect a vacuum source to the side arm of the filter to begin filtration.
7. As long as the mixture passes through the filter, continue to add mixture to the filter bottle. Repeat until the filtration rate becomes very slow.
8. Continue to pull vacuum until the deposited Asphaltene dries enough to form cracks.
9. Turn off the vacuum source. Loosen the bottle-top from the filtrate bottle.
10. Pre-weigh another Bottle-Top filter and repeat steps 5 through 9 until all of the mixture has been filtered.
11. Re-dissolve all of the Asphaltenes including material adhering to filters and surfaces in toluene. Add more toluene and shake the solution vigorously to dilute the solution to a concentration low enough where Asphaltene is not visible under 400x microscope. As a rule of thumb, a concentration of about 0.5-1.0g Asphaltene in 100ml toluene should be adequate.
12. Filter the toluene solution through an 0.22 μ m filter.
13. Concentrate the filtrate with a rotary evaporator to a minimal volume.

14. Estimate the volume of the toluene solution and reprecipitate Asphaltenes with 40 times that volume of the original precipitant.
15. Repeat steps 5 to 10.
16. Place the filtered asphaltene (in the bottle-top filter) on the mass balance and dry in the hood for several days.
17. Check the mass of the bottle-top filter every few hours. If the mass change is less than 0.0001g over a 12-hour period, the Asphaltenes are dry.
18. Determine the mass of Asphaltenes by subtracting the old mass of the bottle top filter from the new mass.
19. Asphaltene content (g/100ml) = $\frac{\text{Mass of dried Asphaltene (g)}}{\text{Crude oil Volume (ml)}} \times 100$

5.2 Wax Appearance Point (WAP)

Wax Appearance Point is that temperature at which wax crystals start to precipitate out of solution under specified cooling conditions. Two different methods are used in this study to measure the wax appearance point of GTL and Crude oil blends. They are: -

- a) ASTM D 3117 Method
- b) Viscometric Method

5.2.1 Wax Appearance Point (ASTM D3117)

5.2.1.1 Materials Used

The equipment used (figure 5.2) consists of: -

1. A double-Walled jacketed sample tube.
2. A number 3, two-hole neoprene rubber stopper. Used in sealing the top of the sample tube.
3. Thermometer: - conforming to specifications for ASTM Thermometer 62C.
4. Vacuum Flask: - An unsilvered vacuum flask of 200mm depth and 65mm internal diameter.

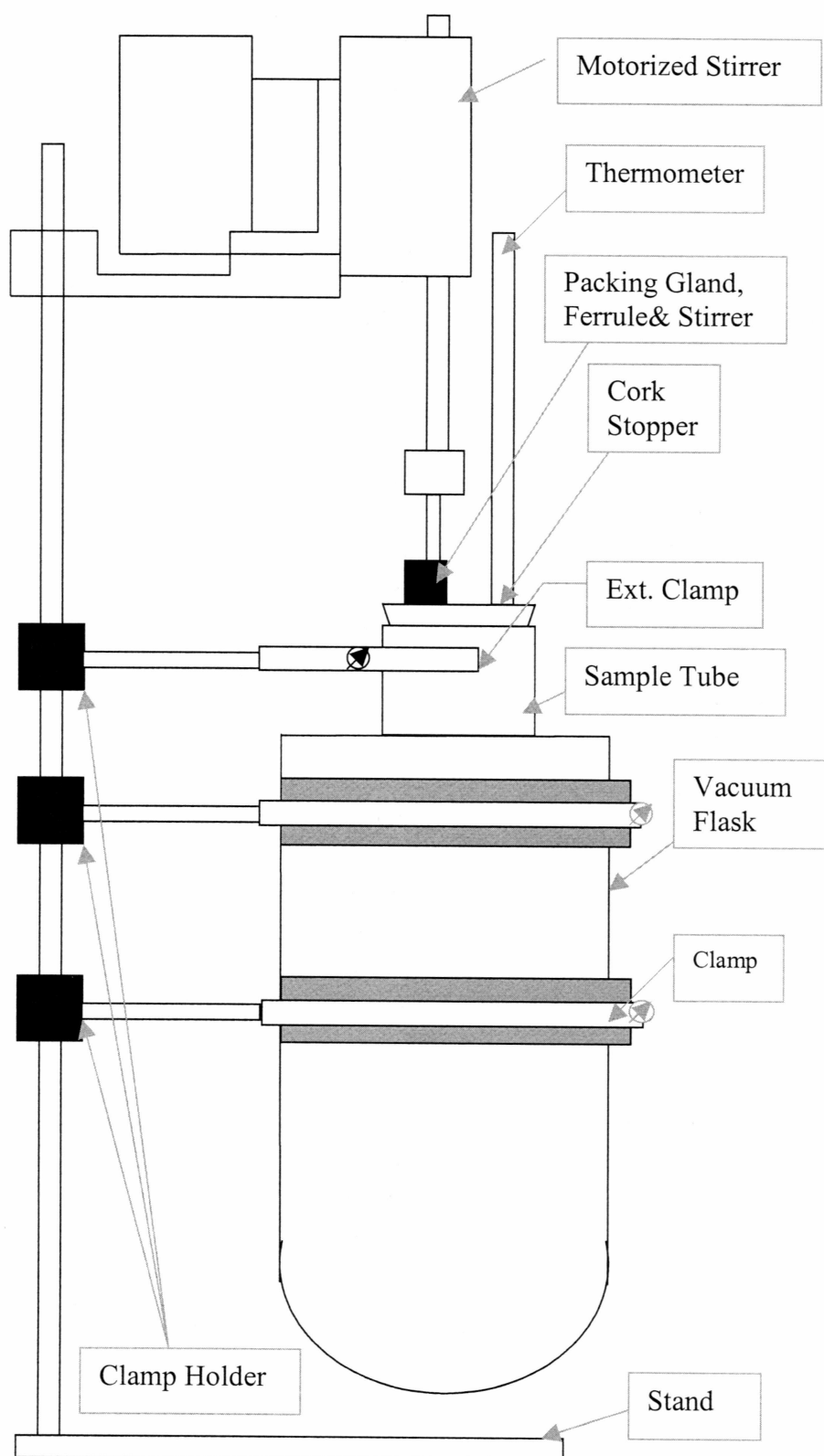


Figure 5.2 Koehler Wax Appearance Point Apparatus

5. Stirrer assembly: - A stainless steel wire (figure 5.3) driven up and down by an electric motor. The frequency of the movement is between 50 to 60 cycles per minute with an amplitude of 50 + or – 5mm.
6. Clock: - Used in monitoring the cooling rate.
7. Carbon Dioxide (Solid) or Dry Ice chips: - Commercial grade dry ice was used.
8. Isopropanol: - Solid carbon Dioxide Chips and Isopropanol formed the mixture for the coolant.

5.2.1.2 Wax Appearance Point Determination Procedure

1. Fix the electric motor with the stirrer assembly firmly on the clamp holder.
2. With the sample at 10°C or above, pipette 25ml of the sample into the sample tube. Add three drops of anhydrous Isopropanol.
3. Adjust the stopper, thermometer, and stirrer so that the bottom of the thermometer is 25mm above the bottom of the sample tube. Ensure that the stirrer does not break the surface at the upper end of its stroke.
4. Start the electric motor when the stopper is firmly seated.
5. Raise the vacuum/cooling flask around the sample tube and start cooling.
6. Adjust the bath height to keep the cooling rate between 1 and 2°C/min.
7. Continue cooling until wax distinctly appears. At this point the wax crystals make a stirring pattern quite obvious.
8. Read and record the temperature at which wax crystals distinctly appeared as the wax appearance temperature.

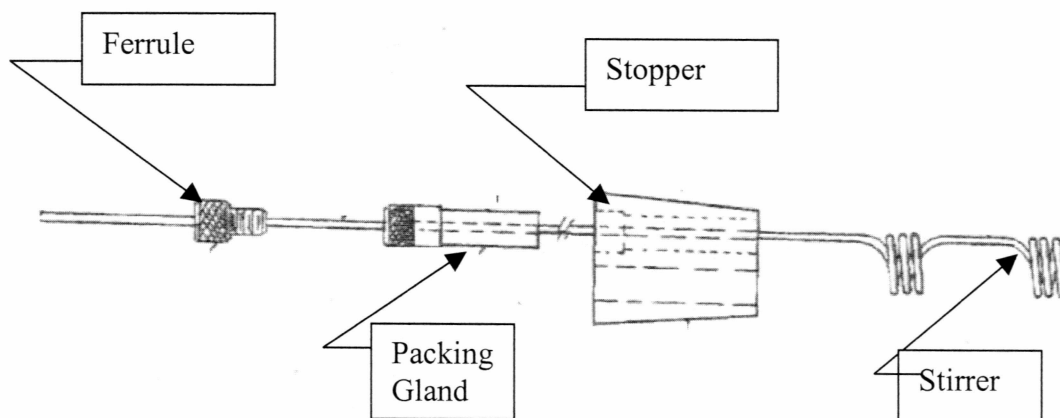


Figure 5.3: Koehler Stirrer Assembly

5.2.2 Wax Appearance Point Determination: Viscometric Method

5.2.2.1 Theory of WAT by Viscometric Method

Theoretically, wax appearance point is that temperature where the first infinitesimally small amount of wax is formed. For Newtonian fluids, viscosity is linearly related with temperature following Arrhenius equation (Hamouda, A.A. et al)

$$\mu = C \exp^{E_a / RT} \quad 5.1$$

Where: -

C = constant dependent on the entropy of activation of flow

E_a = Activation energy of viscous flow

R = Universal gas constant

T = Absolute temperature

When the liquid temperature is below the wax appearance temperature, the fluid becomes non-Newtonian and the viscosity/temperature plot deviates from linearity. Wax appearance temperature is thus determined as the point where deviation from linearity occurs.

5.2.2.2 Equipment Description and Set Up

Brookfield Viscometer model LVDV-II+, figure 5.4, is the apparatus used in all the Viscometric measurements (Wax Appearance Point, and Flocculation Onset Titration) taken in this study. It measures the torque required to rotate an immersed element (Spindle) in a fluid. The spindle is driven by a synchronous motor through a calibrated spring, the deflection of the spring is indicated by a pointer and a digital display. Figure 5.5 shows Brookfield Viscometer setup at University of Alaska Fairbanks.

For a given viscosity, the viscous drag, or resistance to flow (indicated by the degree to which the spring winds up) depends on the spindle's size, speed of rotation, and shape (geometry). Drag increases as the spindle size and/or rotational speed increases. For a given speed and geometry, an increase in viscosity will be indicated by an increase in the deflection of the spring. Minimum range is obtained by using the largest spindle at the highest speed, and the maximum range by using the smallest spindle at the slowest speed. To detect and evaluate the rheological properties of the test fluid, measurements are made using the same spindle at different speeds.

Part of the Brookfield Viscometer is the Small Sample Adapter, figure 5.6, which is a jacketed, coaxial-cylinder accessory that is compatible with all Brookfield Viscometers with the exception of cone-plate types. Depending on the selected model, the Small Sample Adapter utilizes sample volumes ranging from 2.0 to 16.0ml (Table 5.2). Also based on model, the Small Sample Adapter will measure viscosities from 5cp to 10,000,000cps at shear rates from 0.066 to 93.0 reciprocal seconds. The jacketed design of the Small Sample Adapter permits connection to a circulating-type bath for excellent temperature control up to a recommended maximum of 100 °C.

The model is provided with four spindles and a narrow guardleg. The spindle, has left-hand thread, and is attached to the viscometer by screwing it onto the lower shaft. The lower shaft should be secured and slightly lifted with one hand while screwing the spindle to the left. To prevent eccentric rotation of the spindle, the face of the spindle nut and the matching surface on the lower shaft should be clean. A

good procedure to follow is to immerse and position the spindle in the sample fluid before attaching it to the viscometer. The spindle should be immersed up to the middle of the indentation in the shaft. Failure to do so could result in incorrect viscosity reading.

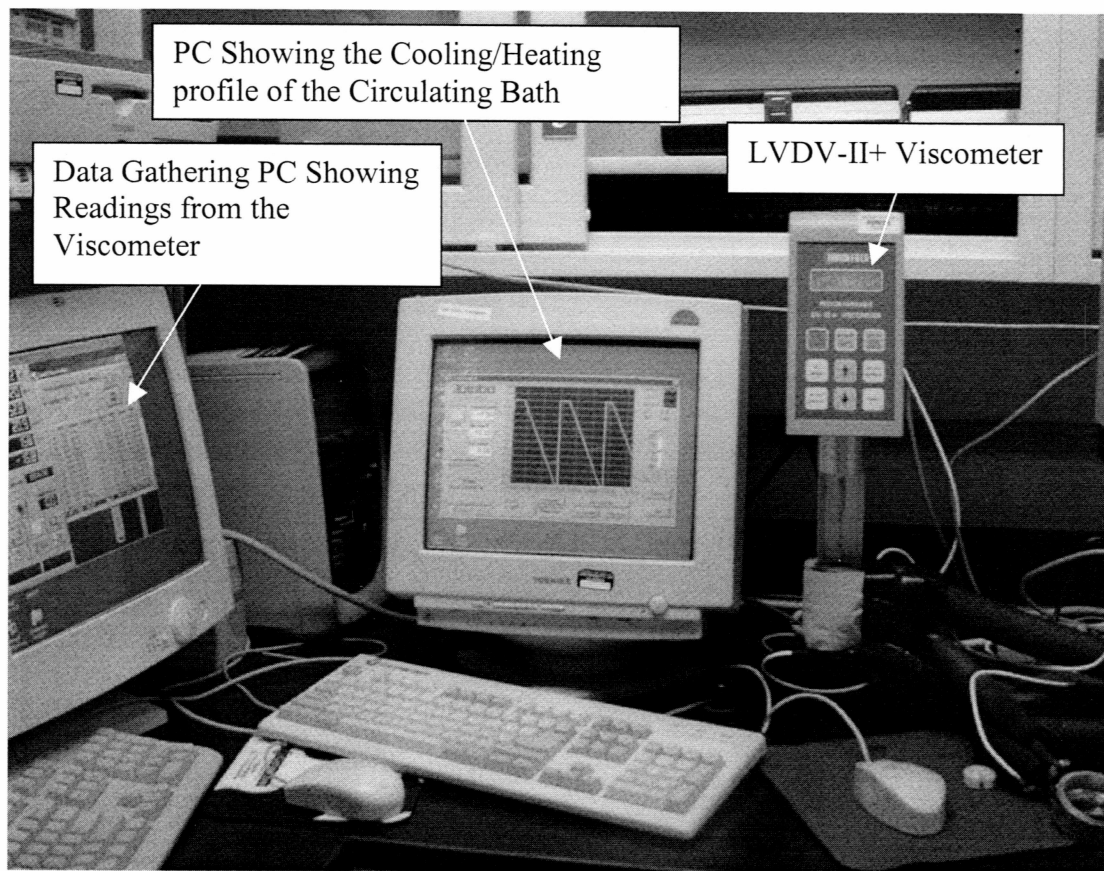


Figure 5.4 LVDVII+ Viscometer in operation

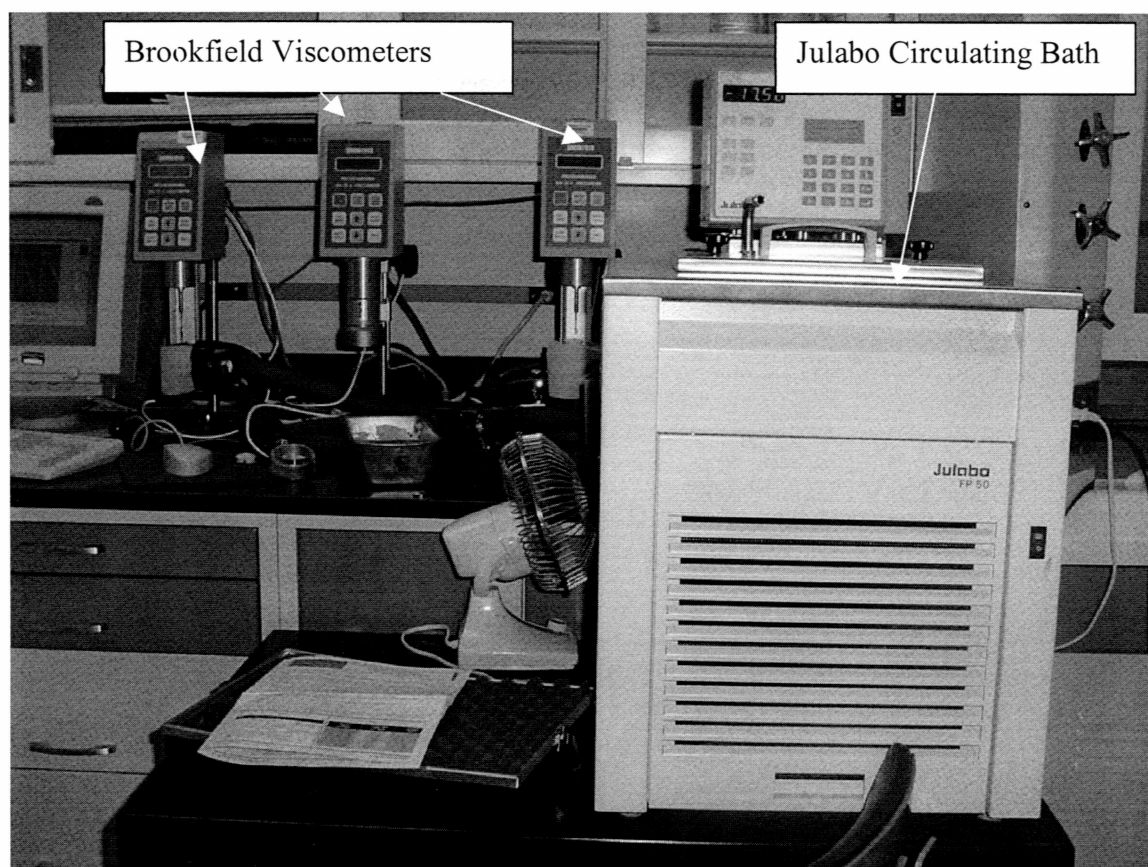


Figure 5.5 Brookfield Viscometer Setup

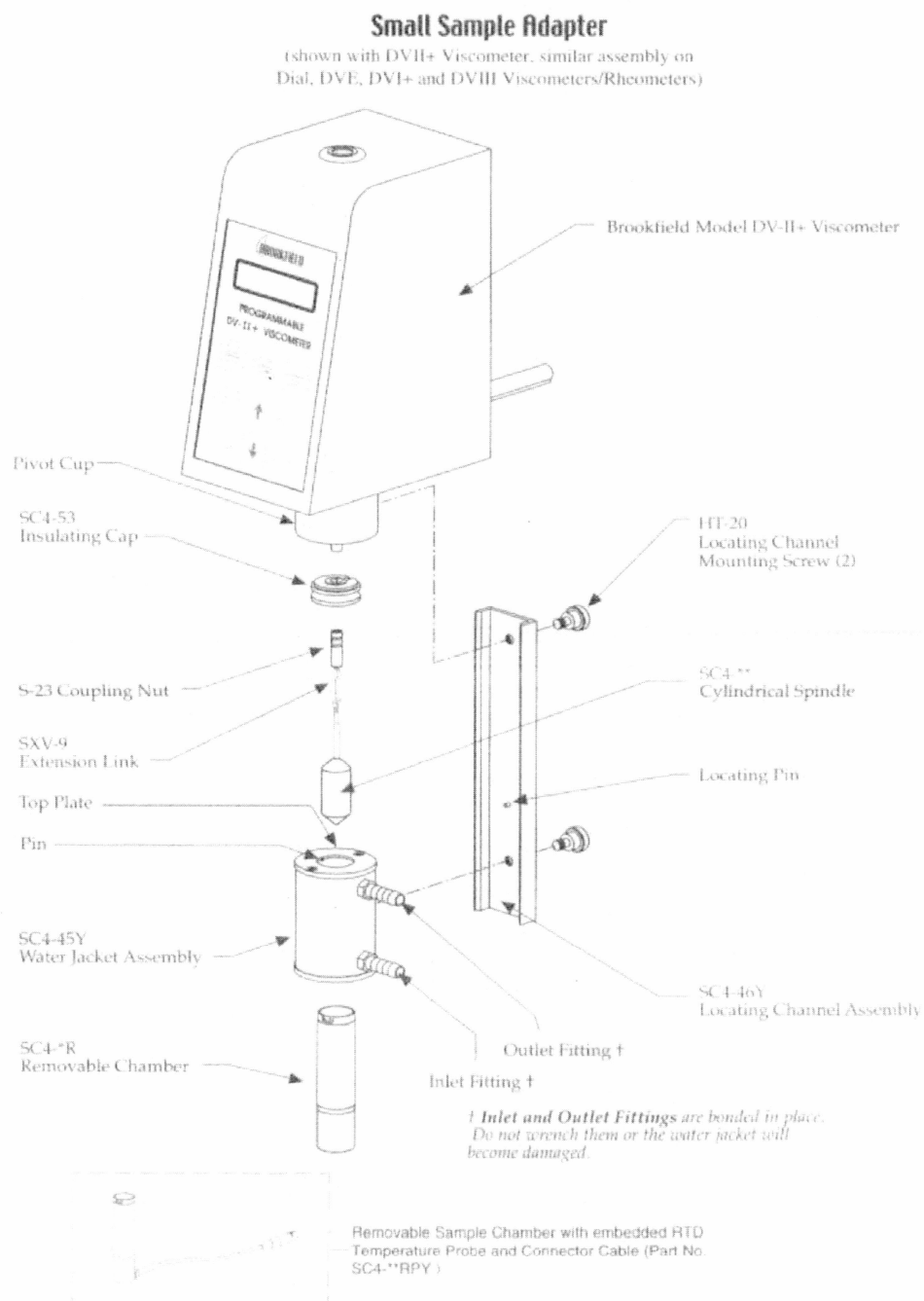


Figure 5.6 Parts of the DVII+ Viscometer with Small Sample Adapter Assembly.

Table 5.2 Spindle/Chamber/Sample Volume Combinations for the LVDV-II+

Spindle	Sample Chamber	Sample Volume	Shear Rate (sec⁻¹)	Viscosity Range
SC4-18	SC4-13RP	8ml	1.322N	1.5-30K
SC4-31	SC4-13RP	10ml	0.34N	15-300K
SC4-34	SC4-13RP	10ml	0.28N	30-600K
SC4-16	SC4-8RP	4.2ml	0.29N	60.1.2M
SC4-25	SC4-13RP	16ml	0.22N	240-4.8M

5.2.2.3 WAP Determination Procedure: Viscometric

1. Power-on the Brookfield LVDV-II+ Viscometer and follow the auto zeroing instructions on the viscometer liquid crystal display (LCD).
2. Turn-on LVDV-II+ data collection computer and open Brookfield WinGather Software.
3. Power on the Julabo Refrigerated circulating Bath and set its temperature to 15°C using the Julabo EastTemp software program installed on the DV-II+ viscometer data collection computer.
4. Verify communication between the viscometer and the data collection computer. If there is no communication, verify the comm. Port and make sure the correct port is being utilized, check the interconnecting cable for proper installation, and check the Options menu and make sure the PC PROG is set to "ON"
5. Remove the sample chamber and pipette 8ml of sample into it. 8ml because SC-18 spindle is used.
6. Insert back the sample chamber into the cooling jacket on the viscometer.
7. Insert the micro thermocouple into the socket at the bottom of the sample chamber.
8. Allow the sample, sample chamber, and spindle to reach the set temperature.
9. Press the "MOTOR ON/OFF" key to start the motor.

10. Select the motor speed based on the expected viscosity range of the sample. Highest speed (200RPM) gives the minimum viscosity range.
11. Program the Julabo refrigerated circulating bath with the desired cold ramp using the EasyTemp software. The desired cold ramp is 1°C/min. To program the circulating bath, select "Edit Profile", Input the desired final temperature in degrees Celsius followed by space and the required chilling time. For example: - To cool a sample from 15°C to -30°C at a cooling rate of 1°C per minute, input **-30.00 00:45**
Where -30.00 is the desired final temperature, 00:45 is the time it will take to cool from 15°C to -30°C.
12. Select "Use Profile". When the current status screen appears, select "Start Profile"
13. Select "Start Gather" button on the WinGather program. The "Start Gather" button is depicted by a viscometer connected to a personal computer.
14. In the "Start Gather" window, select "Timed Stop" and input 1000 into the "Number of Reading" window and 01:00 into the "Time Interval" window. This instructs the software to record data every 60 seconds until 1000 data points are recorded
15. Select "OK" to start the data gathering.
16. Monitor the torque value on the viscometer. Select "Stop" on the WinGather when the torque value is 100% (The viscometer displays "EEEE", indicating that the viscometer has reached its maximum torque potential, or when the sample temperature gets to the set final temperature.
17. Stop the viscometer motor by selecting "MOTOR ON/OFF" on the viscometer keypad.
18. Save the data (selecting Lotus file*wks, will allow easy inputting of data into Microsoft Excel)
19. Set the temperature of the refrigerated circulating bath to 15°C, this melts the wax and allows for easy cleaning.

20. Disconnect the spindle. Remove the sample chamber with sample waste and spindle.
21. Dispose the sample waste into a hazardous material collection container. Clean the sample chamber, and spindle thoroughly with toluene. Displace the toluene away with an application of acetone. Dry the sample chamber and spindle with compressed dry air, ensuring that no toluene or acetone remains to contaminate future samples.
22. Using the saved data, plot viscosity against temperature.
23. The kick off on the plot is the wax appearance temperature.

5.3 Flocculation Onset Titration (Viscometric Method)

This technique analyzes the trends of suspension viscosities as a function of precipitating solvent concentration. Through accurate measurements of viscosity of crude oil upon titration with a precipitating agent, the onset of Asphaltene flocculation is determined. This method is based upon experimental observations of an increase in the viscosity of a crude oil-Asphaltene-flocculating agent suspension in which asphaltene particle aggregation occurs. The onset of Asphaltene flocculation is detected graphically as the change in the trend of the curve. This technique is used in this study to determine the onset of Asphaltene flocculation of ANS crude using GTL, n-heptane, and n-pentane as a flocculant.

5.3.1 Flocculation Onset Titration Determination Procedure

1. Power-on the Brookfield LVDV-II+ viscometer and follow the auto zeroing instructions on the liquid crystal display (LCD).
2. Turn-on the LVDV-II+ data collection computer and open Brookfield Wingather software.
3. Power on the Julabo refrigerated circulating bath and set its temperature to 21°C using the Julabo EasyTemp software program installed on the DV-II+ viscometer data collection computer.

4. Verify communication between the viscometer and the data collection computer. If there is no communication, verify the comm. Port and make sure the correct port is being utilized, check the interconnecting cable for proper installation, and check the Options menu and make sure the PC PROG is set to "ON"
5. Remove the sample chamber and pipette 5ml of sample into it. 5ml so as to allow the titration of the flocculant into it. Use SC-18 spindle.
6. Insert back the sample chamber into the cooling jacket on the viscometer.
7. Insert the micro thermocouple into the socket at the bottom of the sample chamber.
8. Allow the sample, sample chamber, and spindle to reach the set temperature.
9. Press the "Motor ON/OFF" key to start the motor
10. Select the motor speed. It is recommended to select speed so that the percentage torque will be high since the titration will reduce the torque.
11. Select "Start Gather" button on the Wingather program. The "Start Gather" button is illustrated by a viscometer connected to a personal computer.
12. In the "Start Gather" window, select "Timed Stop" and input **1000** into the "Number of Reading" window and **0.1:15** in the "Time Interval" window. This instructs the software to record data every 75 seconds until 1000 data points are recorded.
13. Select "OK" to start the data gathering.
14. Wait for 75 seconds for the first data collection, and then titrate 0.05ml of the flocculant (may be GTL, n heptane, n-pentane or non-flocculant (toluene)) into the sample chamber.
15. Wait for another 75 seconds for the data to be collected by the computer before titrating again.
16. Repeat step 15 until the required volume of the flocculant has been titrated into the sample chamber.

17. Upon the end of the titration wait for another 75 seconds for the data to be collected and then stop the Wingather.
18. Save the data (selecting Lotus file*.wks, will allow easy inputting of data into Microsoft excel)
19. Disconnect the spindle. Remove the sample chamber with sample waste and spindle.
20. Dispose the sample waste into a hazardous material collection container. Clean the sample chamber, and spindle thoroughly with toluene. Displace the toluene away with an application of acetone. Dry the sample chamber and spindle with compressed dry air, ensuring that no toluene or acetone remains to contaminate future samples.
21. Using the saved data, plot viscosity against volume of flocculant in solution.
22. Note the change in the trend of the curve as the onset of Asphaltene flocculation.

5.4 Flocculation Onset Titration: Stability Test

This is done by performing titrations of a toluene solution of the Crude oil sample with heptane. At each titration point, the time required for a given quantity of the fluid to pass through a narrow channel of the cannon-fenske viscometer is measured. This time is related to the fluid viscosity.

5.4.1 Equipment Used

The equipment used, as shown in figures 5.7 and 5.8, consists of: -

- a. Cannon-Fenske Viscometer
- b. Constant Temperature Bath
- c. Stop Clock
- d. Mass Balance

5.4.2 Stability Test Procedure

1. Blend the required concentration of crude oil dissolved in toluene.
2. Invert the viscometer immerse tube "A" into the sample blend and apply suction to "J". This causes the sample to rise to the etched line "E".
3. Turn the viscometer upright and wipe tube "A" clean.
4. Insert the viscometer into a holder and place in a Constant temperature Bath. Allow 10 minutes for the viscometer to reach the set temperature of the bath.
5. Apply suction to tube "A" and bring sample a short distance above mark "C". Measure the efflux time by allowing the sample to flow freely through mark.

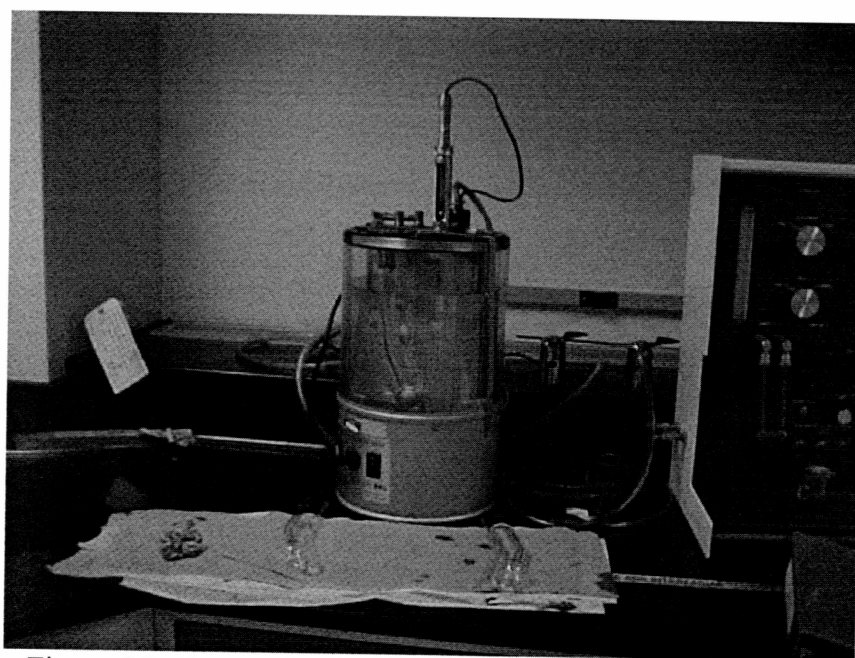


Figure 5.7: Cannon-Fenske viscometer in Constant Temperature Bath

6. "C", measuring the time for the meniscus to pass from "C" to "E".
7. Titrate 0.05ml of n-heptane into tube "A"
8. Apply suction to tube "J", for proper mixing of the sample with the heptane.
9. Repeat steps 5 and 6 for each titration.
10. Plot time against volume of n-heptane and mark the point where there is an observed change in trend as the onset point.

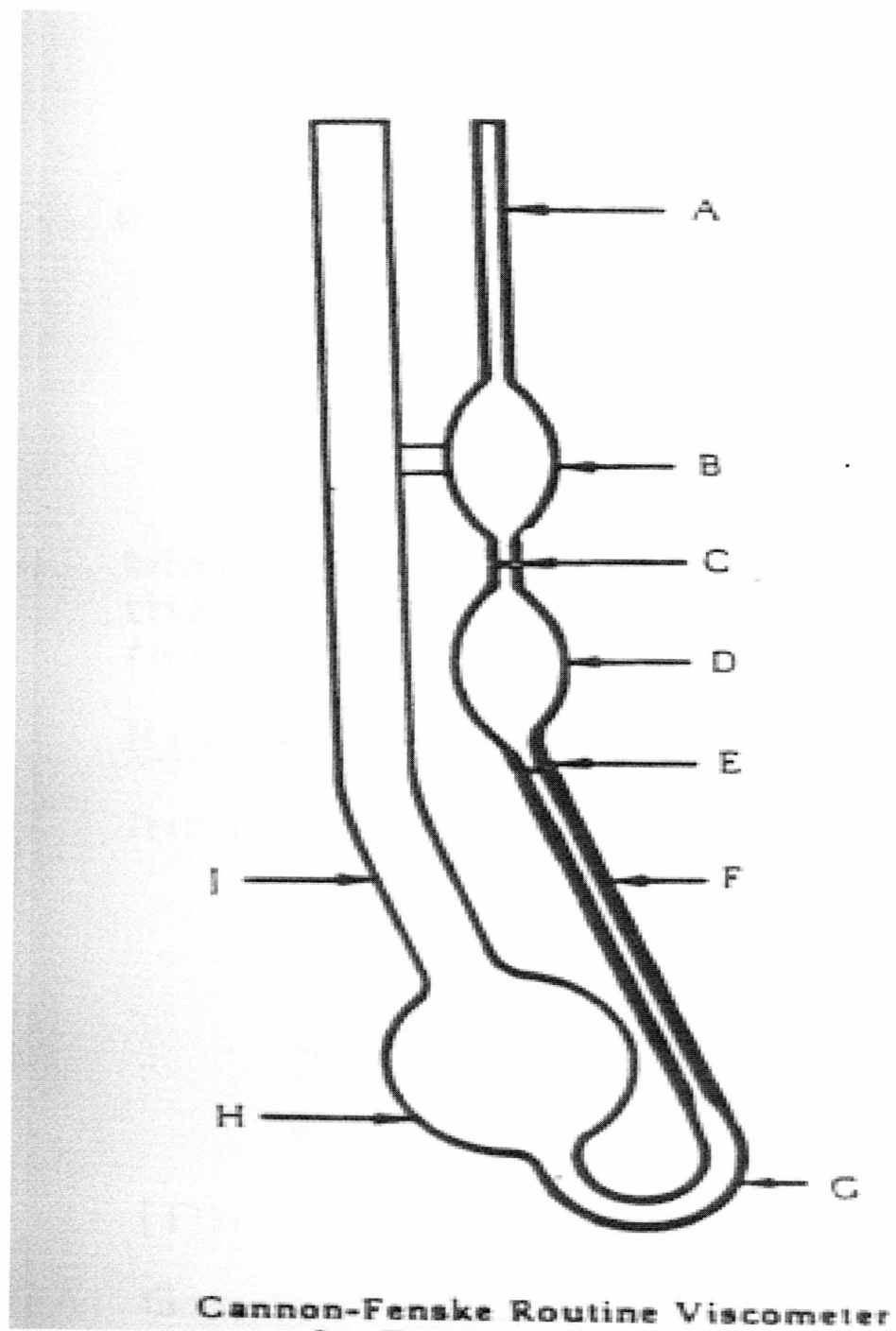


Figure 5.8: Cannon-Fenske Viscometer

5.5 Reid Vapor Pressure Measurement

The Reid Vapor Pressure of the samples were determined by Alyeska Pipeline Service Company at Valdez Analytical laboratory.

5.5.1 Equipment and Materials Used

- a) Vapor pressure test apparatus
- b) Ice bath for cooling sample cylinder, gasoline chambers, and n-hexane standard
- c) Herzog semiautomatic vapor pressure analyzer
- d) Certified bath thermometer
- e) Hexanes
- f) Turbine fuel
- g) n-hexane, 99mol%

5.5.2 Reid Vapor Determination Procedure

The following procedure is adapted from Valdez Analytical Laboratory Procedure.

1. Fill the bath with distilled water above the lower line inscribed on the thermometer well in the back of the bath.
2. Verify that all gauges read zero ± 0.05 psig
3. Verify that the gauge fittings are tight.
4. Power on the Herzog analyzer by pushing the MAIN SWITCH button. Also push the white STIRRER button to begin circulating and heating the water.
5. Push the yellow START/TROUBLE reset button to start the analyzer.
6. After about 30 minutes, the bath will be ready and the "0" LED becomes illuminated. Verify that the bath temperature is 100°F (37.8°C) using a certified thermometer (ASTM 18F).

7. If the bath temperature is not 100°F (37.8°C) as measured by the certified thermometer when the “0” LED is showing, make the adjustments to the measured bath temperature using the small TEMP adjustment potentiometer above the LEDs
8. If adjustments are made, wait for the temperature to stabilize before proceeding.
9. Place the air chambers (two for the duplicate sample runs and one for the hexane quality control standard)
10. Place the filled sample cylinder and three clean gasoline chambers into the ice water bath, and cool to 30°F (0°C). Also suspend a sealed bottle of n-hexane standard in the ice water bath at this time.
11. After 30 minutes, remove each air chamber from the analyzer bath and allow the water to drain out.
12. Screw the tee-handle fitting with the spiral hose onto the non-knurled (shiny) end of each air chamber and return them to the analyzer water bath.
13. After a minimum of one hour, remove the chilled sample cylinder from the ice bath and attach it to the support stand in a vertical orientation.
14. Quickly empty the water from two of the chilled gasoline chambers and place them close to the lower valve of the sample cylinder.
15. Immediately open the bottom valve of the sample cylinder to start the flow of sample into a beaker or directly into the solvent sink. Open the valve at the top of the sample cylinder only as often as necessary to maintain flow. Discard any free water that might have condensed in the cylinder.
16. Fill one of the gasoline chambers to overflowing.
17. Remove the air chamber and tee-handle assembly from the analyzer bath and quickly drain. Drain briefly and without shaking.
18. Immediately attach the air chamber to the gasoline chamber. The connection should be tight to prevent leaking into the analyzer bath water. Do the

connection without undue movements through the air that could promote exchange of room temperature air with the 100°F air in the chamber.

19. Immediately repeat the process to fill the second gasoline chamber and attach it to the second air chamber and the tee-handle assembly.
20. Rinse off excess crude oil from the test equipment with hexanes before proceeding.
21. Remove the chilled n-hexane standard from the water bath as well as the last chilled gasoline chamber.
22. Fill the gasoline chamber to overflowing with n-hexane and quickly couple it to the air chamber tee-handle assembly in a manner similar to that for the samples. Wipe excess n-heptane from the test equipment before proceeding. This will serve as the quality control check standard.
23. Attach the quick-disconnect hose fitting of each test apparatus to the appropriate gauge port.
24. Tilt the chamber assembly approximately 30 degrees toward the end with the spiral hose and rotate gently to facilitate the flow of crude into the air chamber.
25. Do not allow the crude to enter the spiral tubing.
26. Place the test apparatus (the air and gasoline chambers) into the water bath so that the right end of the gasoline chamber fits into the circular guide on the right end of the reservoir, and the neck of the tee-handle hose fitting rests in the Teflon cradle. (The apparatus may have to be rotated until it fully seats into the circular guide.)
27. Push the white TEST button to start the motor. This will rotate the test chambers back and forth to provide gentle agitation and constant temperature.
28. Check the initial indication on each pressure gauge. Read and record the pressure on each gauge after 25 minutes, then every 3 minutes, or until two stable consecutive readings are obtained. The sample and hexane standard

gauges should be read to the nearest 0.05 psi (based on ASTM method D323-82)

29. Calculate the average of the duplicate sample results, and report the final vapor pressure result to 3 significant figures.
30. Report the final vapor pressure result for the n-hexane standard to the nearest 0.05 psig. Absolute vapor pressure of n-hexane is 4.96 psig
31. Upon completion of the test, push the white "TEST" button to stop the motor, then push the green "MAIN SWITCH" button to turn off the power.
32. Remove the tubing quick-disconnect from the gauge ports.
33. Remove each test apparatus from the bath and stand it up on its end for about 5 minutes so that the crude oil drains back into the gasoline chamber.
34. Loosen the tee-handled screw coupling from the air chamber near the hood and allow the vapors to escape.
35. Separate the gasoline chamber from the air chamber and discard the crude oil.
36. Rinse out both chambers with turbine fuel, then hexanes. After the hexanes have evaporated, wash the chambers in the laboratory dishwasher. Allow the chambers to air dry prior to storing them until next analysis.
37. Clean out any crude oil from inside the spiral tubing and tee-handled fitting. You may remove the quick-disconnect from the tubing in order to do this.
38. Drain the crude oil from the sample cylinder, wipe off any excess oil on the outside of the cylinder, and return cylinder to storage stand.

CHAPTER 6

RESULTS AND DISCUSSIONS

6.1 Static Asphaltene Test

The first issue to address is whether the Alaska North Slope (ANS) crude is asphaltenic or not. Using Petroleum Resources Research Center (PRRC) Standard 02-02: Standard Procedure for Separating Asphaltenes from Crude oils, the following results as shown in table 6.1 were obtained.

Table 6.1 Asphaltene Content of ANS with different Precipitants

Precipitant	Asphaltene Content (g/100ml)
N-Heptane	2.65
N-Pentane	3.7
Raw GTL	1.9
302 GTL	1.35
254 GTL	1.65

The table shows that Alaska North Slope Crude (ANS) contains Asphaltene, and that GTL is a possible precipitant of Asphaltene, though not as strong a precipitant as n-heptane and n-pentane. The quantity of Asphaltene precipitated from 254cut is higher than that from 302 cut, this shows that the light ends are responsible for Asphaltene flocculation/precipitation. Raw GTL has more light ends than either 254 or 302 (some light ends are lost during distillation); this explains why it has higher Asphaltene precipitate than either 254cut or 302cut.

6.2 Flocculation Onset Titration

Viscometric method of flocculation onset titration is used. Two known flocculants (n-pentane and n-heptane), a known non-flocculant (Toluene), and GTL are used in the test. The test results are shown graphically in figure 6.1.

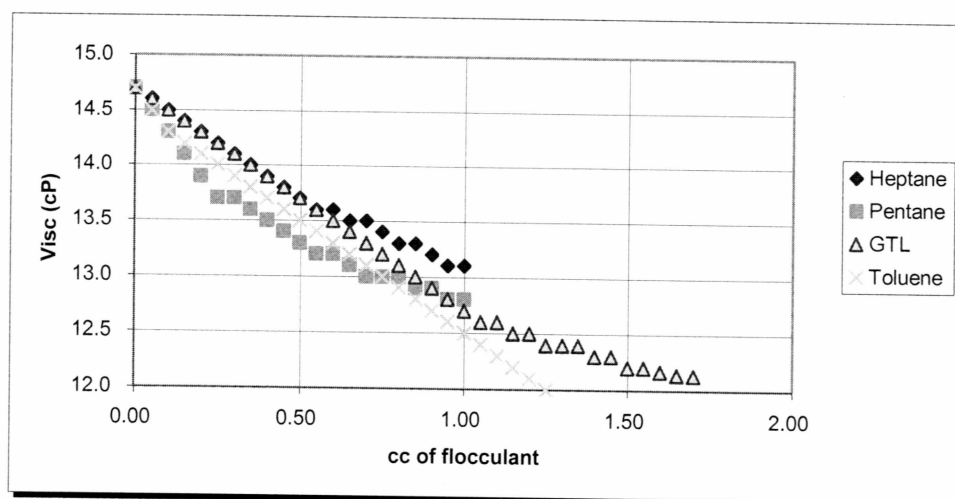


Figure 6.1 Flocculation Onset Titration Results

At the flocculation point, there occurs a change in slope. As can be seen from the toluene curve, there is no change in slope indicating that toluene is a non-flocculant. For GTL, n-Pentane, and n-Heptane there is an observable change in slope indicating that they are flocculants of Asphaltene. This therefore indicates that blending GTL with crude oils will have the possibility of flocculating Asphaltenes. With 5ml of crude oil flocculation occurred when 1.05 ml of GTL is titrated indicating that as low as 3:1 crude oil/GTL ratio, Asphaltene flocculation is a possibility.

6.3 Stability Test

The stability of Asphaltenes in oil samples can be analyzed by performing titrations of a toluene solution of the oil sample with a non-solvent or precipitant like heptane (Dandekar, et al, 2000). This technique also analyzes the trends of suspension viscosities (represented by the efflux time) as a function of precipitating solvent

concentration. Through accurate measurements of efflux time of crude oil/toluene mixture upon titration with a precipitating agent, the onset of Asphaltene flocculation is determined. Two more titrations are made; each with different concentrations of oil dissolved in toluene in order to account for the dilution effects. According to a general practice, a plot of precipitant/mass of oil (flocculation point) versus the solvent/mass of oil will plot linear revealing the stability of the Asphaltenes in the neat undiluted oil. The slope of the flocculation analysis plot is related to the Asphaltene properties as a solute, and the y-axis intercept is a measure of the solubility power of the oil phase towards Asphaltene (Dandekar, et al, 2000). Positive intercept indicates stability while negative intercept indicates otherwise. The results are shown in figures 6.2 to 6.5.

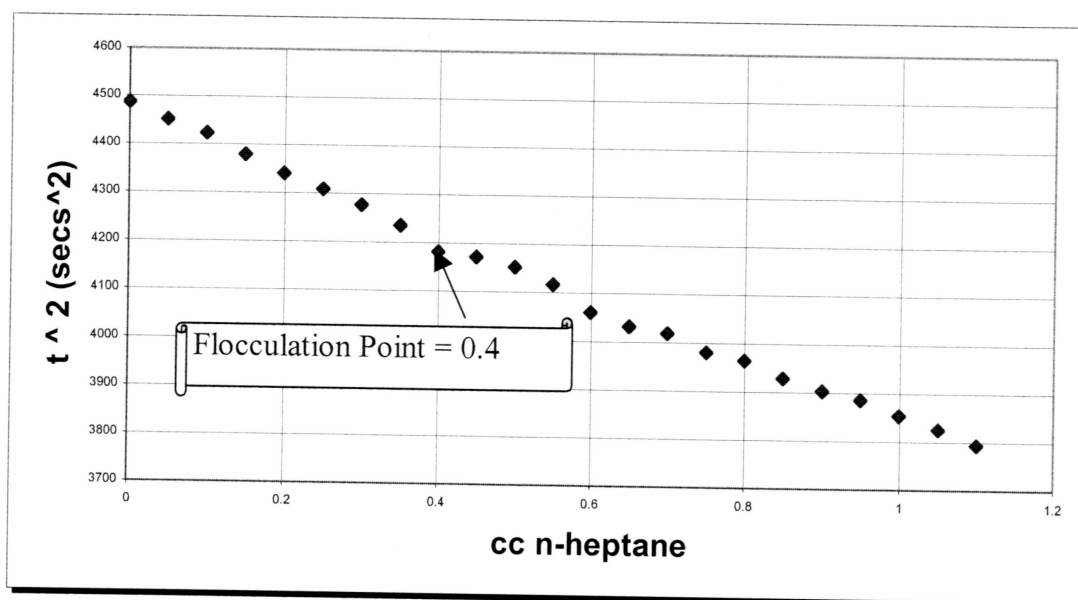


Figure 6.2: 1 cc Toluene per gram of Oil.

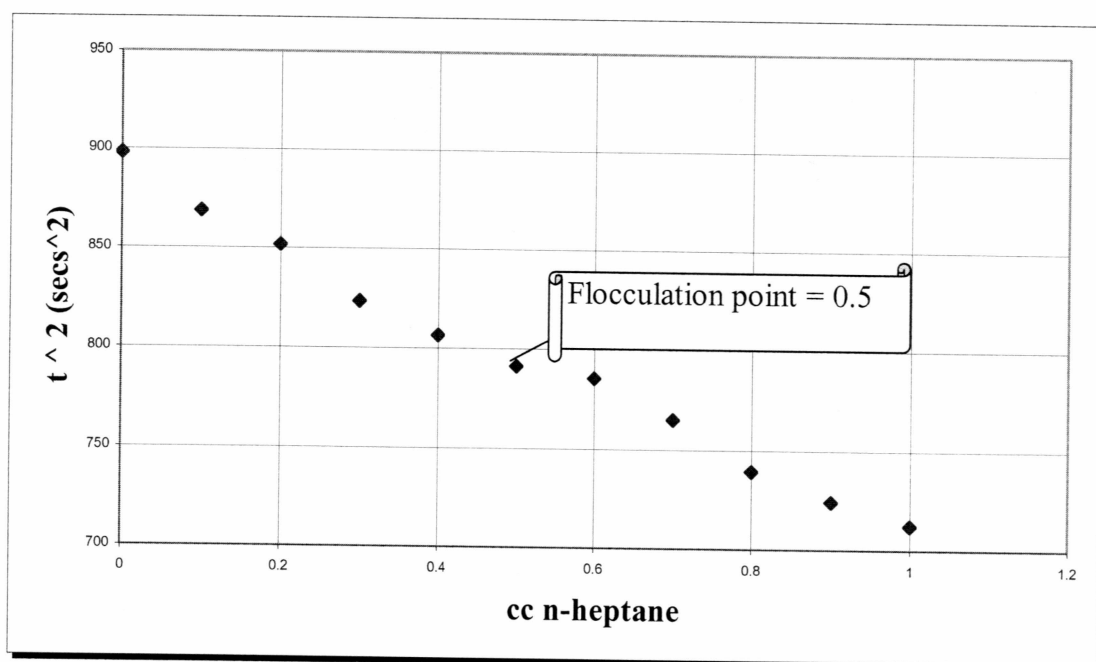


Figure 6.3: 2cc Toluene per gram of Oil

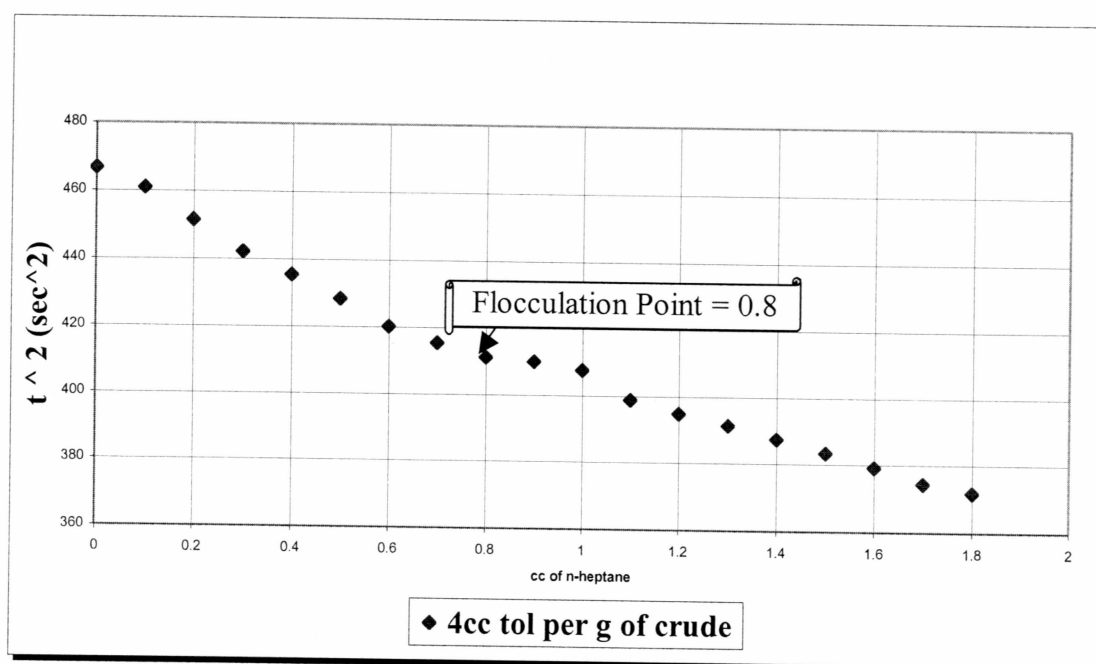


Figure 6.4: 4cc Toluene per gram of Oil

From the graphs above, table 6.2 is obtained.

Table 6.2: Flocculation Point of ANS Crude Oil at Different Toluene Concentrations

Toluene Concentration cc/gram of crude oil	Flocculation Point
1	0.4
2	0.5
4	0.8

Plotting flocculation point against toluene concentration gives the figure below:

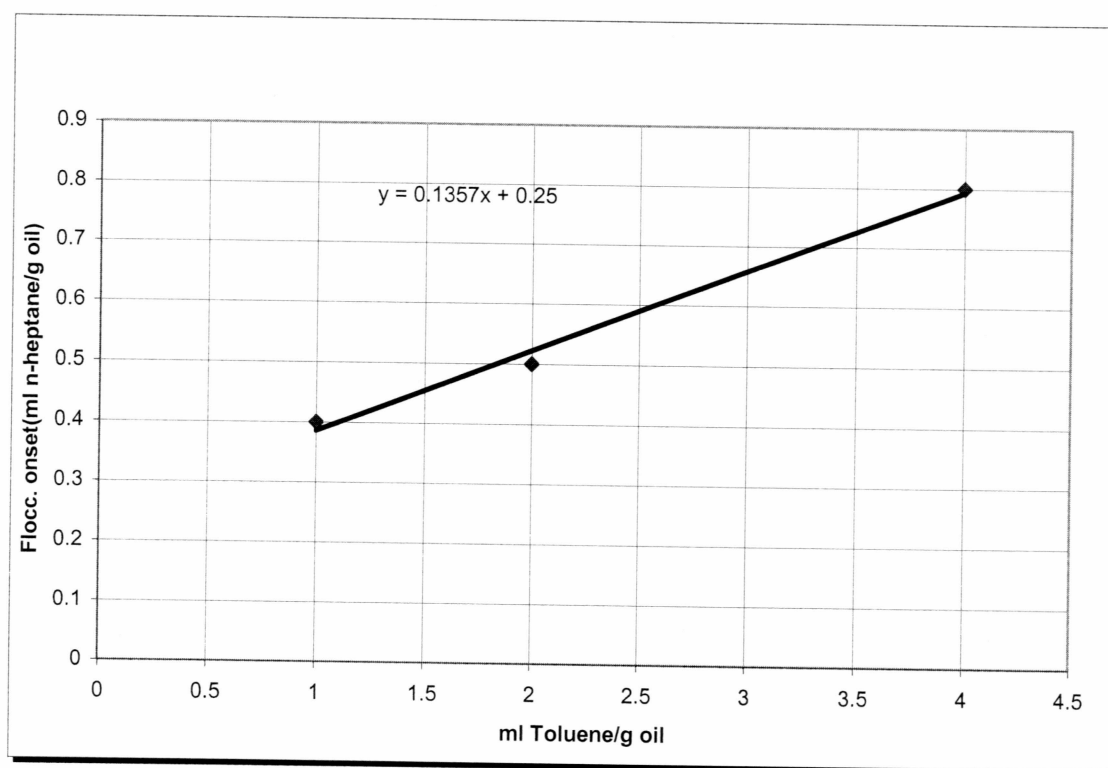


Figure 6.5 Stability Plot for ANS Crude

As seen in figure 6.5, the graph has a positive intercept of 0.25. This shows that Alaska North Slope Crude is stable to Asphaltene deposition. It is capable of suspending Asphaltenes in solution without dropping.

6.4 Wax Appearance Temperature

Two separate methods are used in this study to determine the wax appearance temperature of various cuts of GTL and GTL/Crude oil blends; the methods are ASTM D3117 standard and Viscometric method. The ASTM method is a visual approach and can be used only on clear fluids like GTL but not on black oils. The result from the ASTM method is shown in table 6.3 and figure 6.6.

Table 6.3 WAT of Various Cuts of GTL: ASTM D3117 Standard

GTL	Temperature (°F)
254 Cut	-12
302 Cut	5
344 Cut	24
FT Diesel	30
Raw GTL	48

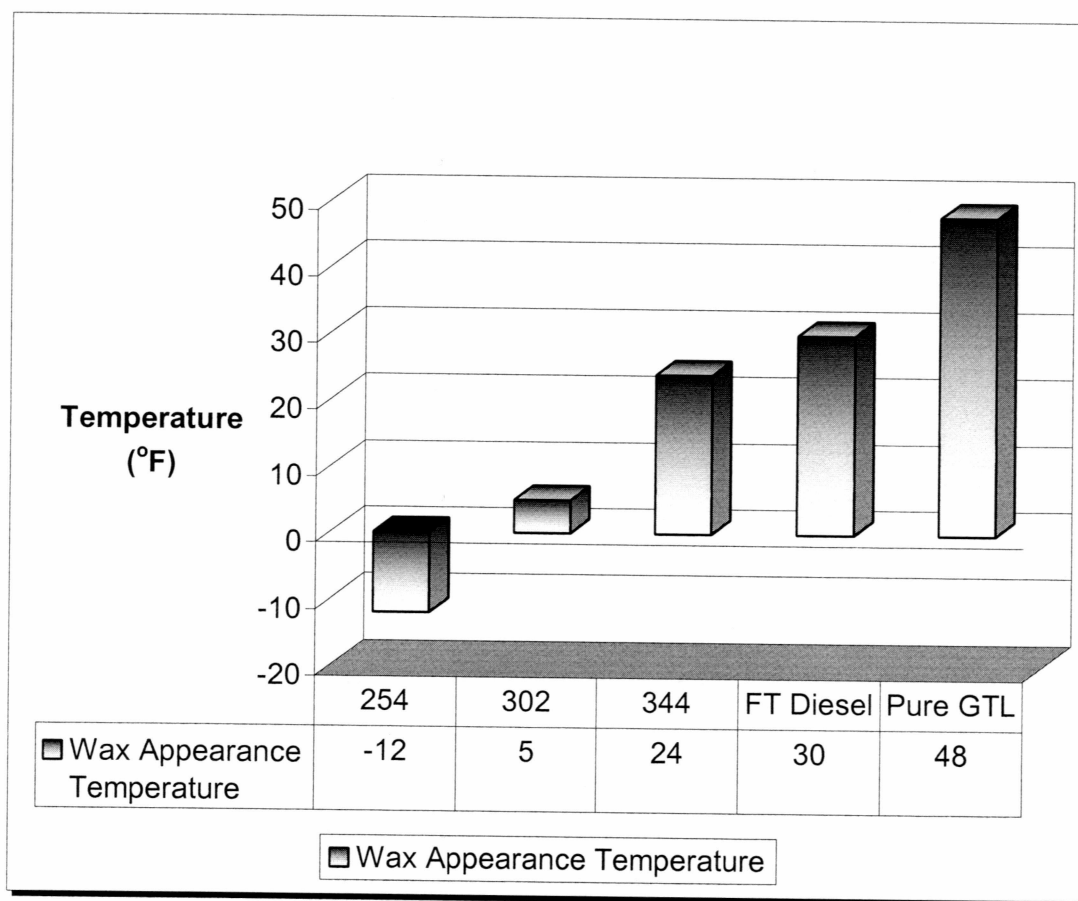


Figure 6.6: WAT of Various Cuts of GTL: ASTM D3117 Standard

The plot showing the Wax Appearance Temperature of each of the samples, using Viscometric method is presented in figures A.1 to A. 14 in the appendix. Table 6.4 and figure 6.7 show the summary of the Wax Appearance Temperature, using Viscometric method, of the test fluids used in this analysis.

Table 6.4: WAT of Various Blends of Crude Oil/GTL: Viscometric Method

Sample	Wax Appearance Temperature °F
Raw GTL	48.0
1:1 Crude oil/Raw GTL	44.4
Crude Oil	43.7
3:1 Crude oil/FT Diesel	42.3
3:1 Crude oil/344 Cut	41.2
3:1 Crude oil/302 Cut	39.7
3:1 Crude oil/254 Cut	38.6
1:1 Crude oil/344 Cut	36.7
FT Diesel	30.1
1:1 Crude oil/302 Cut	24.4
344 Cut	23.4
1:1 Crude oil/254 Cut	10.4
302 Cut	4.1
254 Cut	-11.6

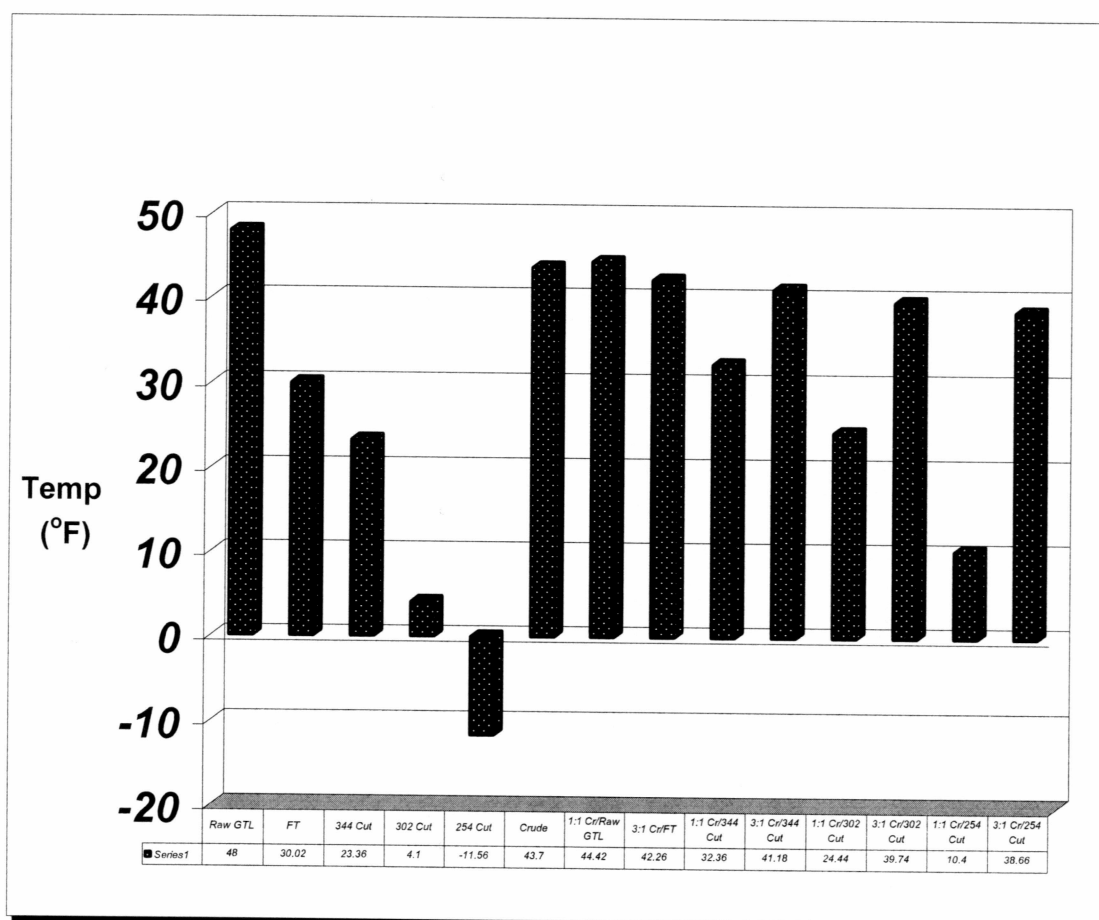


Figure 6.7: WAT of Various Blends of Crude oil/GTL using Viscometric Method

The results show that raw GTL has the highest WAT of 49°F. Blending the crude oil with lower boiling point cuts of GTL lowers the Wax Appearance Temperature of the fluid. Thus for pipeline temperature of 49°F, GTL of lower boiling point should be used.

To validate the Viscometric method of WAT determination, standard liquids of known WAT were used and their results are shown in figures 6.8 to 6.11.

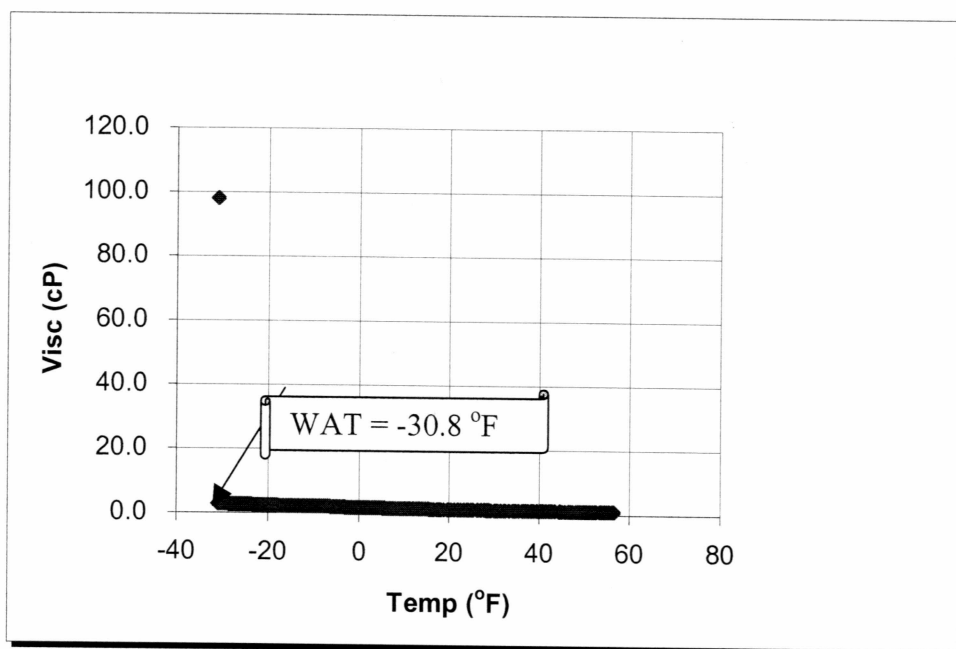


Figure 6.8 WAT of n-Decane

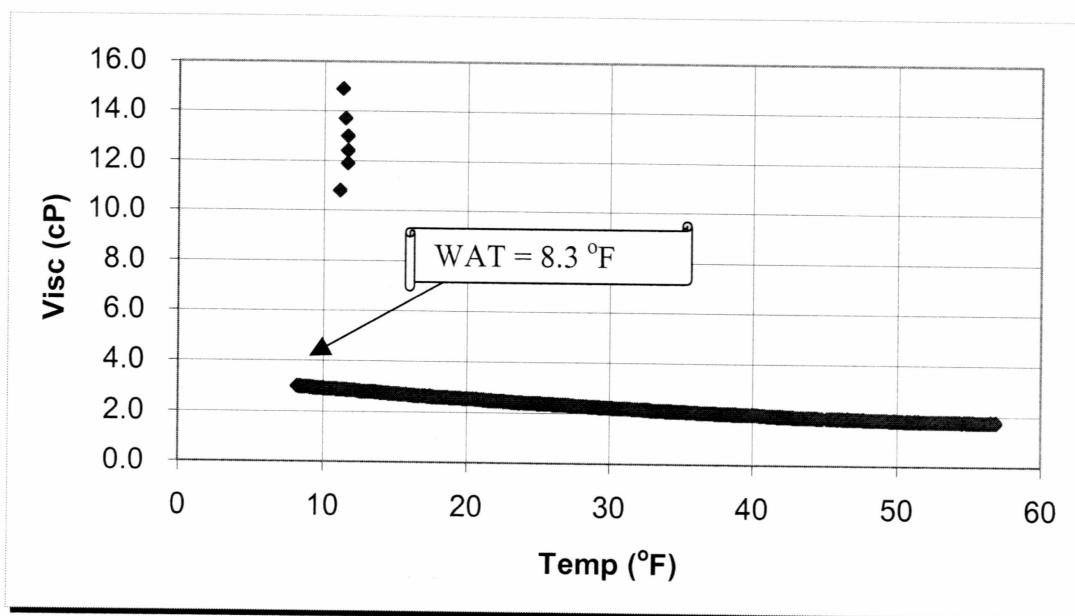


Figure 6.9 WAT of n-Dodecane

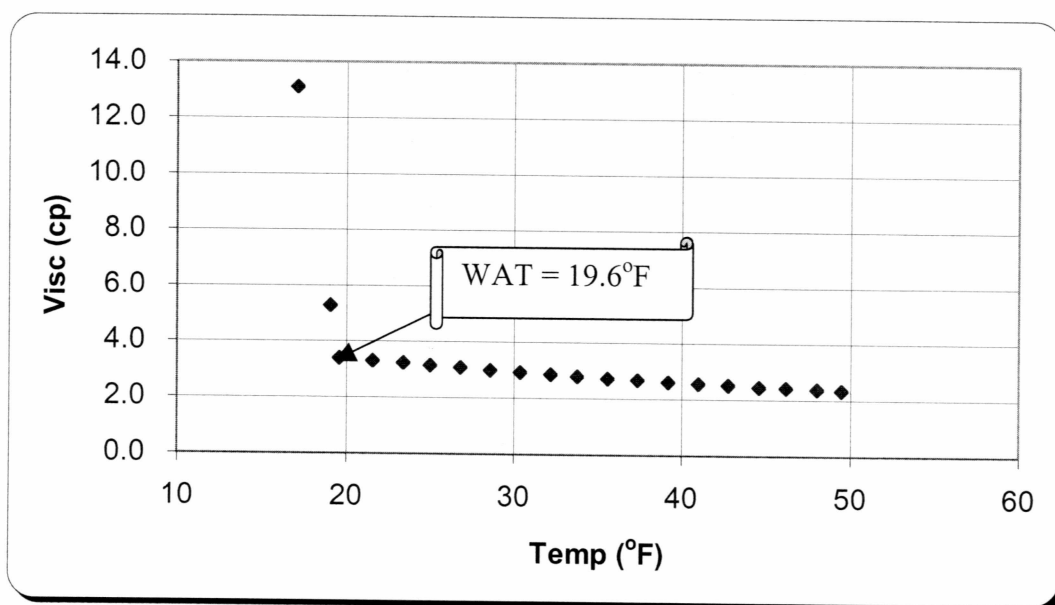


Figure 6.10 WAT of n-Tridecane

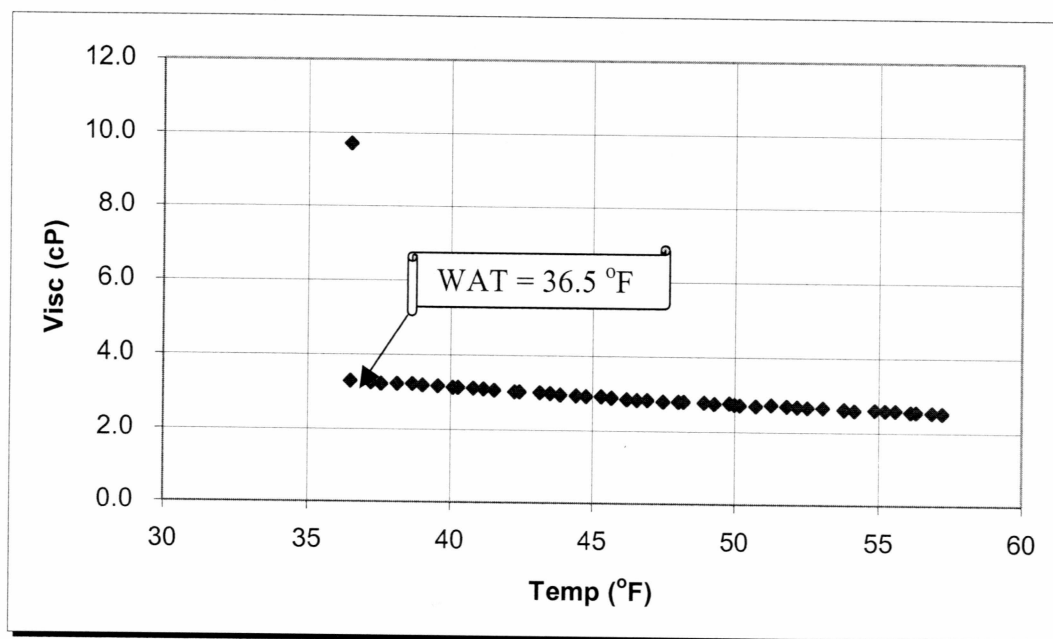


Figure 6.11 WAT of n-Tetradecane.

The results from these pure components agree with the published wax melting temperature data of the components, figure 6.12 and table 6.5. It should be noted that

though wax appearance temperature (WAT) is close to wax melting temperature (WMT), WAT is always lower than WMT. Therefore with the Viscometric method the wax appearance temperature of both clear and dark liquids can be measured accurately.

Table 6.5: Comparison of WAT and WMT of the Pure Components.

	WMT (TCI Material Safety Data Sheet) °F	WAT °F
n-Decane	-22	-30.8
n-Dodecane	14.7	8.3
n-Tridecane	24.8	19.6
n-Tetradecane	41.9	36.5

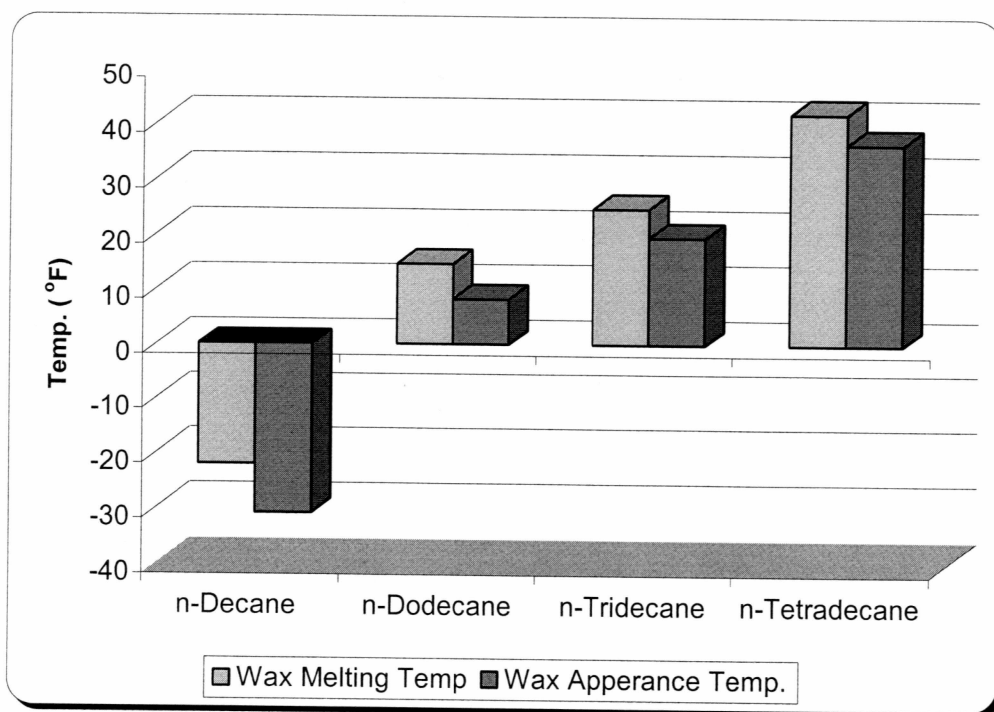


Figure 6.12: Comparison of WAT and WMT of the Pure Components.

6.5 Reid Vapor Pressure

GTL and Crude Oil/GTL blends in the ratio of 3:1 and 1:1 were prepared and sent to Valdez for RVP testing, the results are shown in figure 6.13. However, the results are not consistent and cannot be relied upon because the GTL samples we are working with do not meet the requirements for RVP tests. Samples have been drawn from the raw GTL container for other tests over the past years, and also because of the fact that the GTL in the container at the time of this test is less than 40 percent of the container volume. Thus the sample has lost most of its volatile ends. Based on ASTM and IP standards RVP test should not be done if more than one sample has been taken from the sample container, and/or if the sample in the container is less than 80 percent volume of the container. Therefore for reliable RVP results new samples in well-preserved containers are needed.

Specifically both ASTM D323 and IP69 standards, states that Reid Vapor test shall be performed on the first test specimen withdrawn from the sample container, the remaining sample in the container cannot be used for a second vapor pressure determination. The sample container and contents shall be cooled to 0 to 1°C before the container is opened. The sample container shall be at least 80% filled with sample. None of these conditions is met by the sample considered in this test.

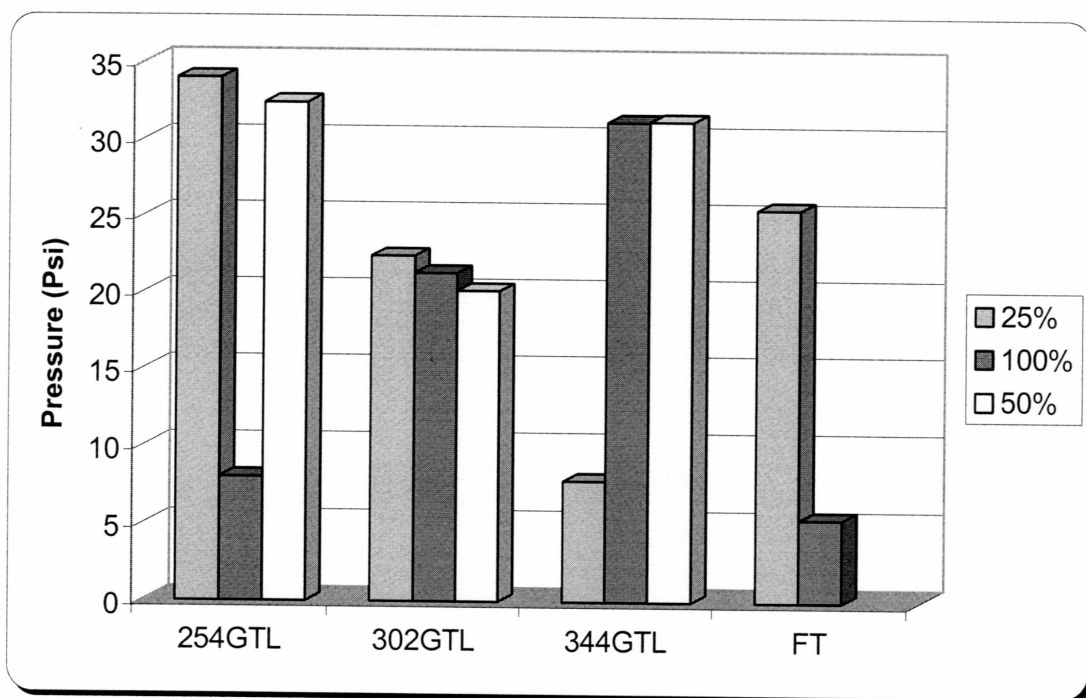


Figure 6.13 Vapor Pressure of GTL Cuts and GTL/Crude Oil Blends at 200 °F

CHAPTER 7

CONCLUSION AND RECOMMENDATION

7.1 Conclusions

Based on the results presented in this study, the following conclusions are drawn: -

- GTL has the tendency to flocculate Asphaltenes, as a result of its light ends; therefore blending the products in commingled mode will result in Asphaltene flocculation and deposition.
- GTL is not as strong a precipitant as n-pentane or n-heptane.
- ANS crude is a stable crude in terms of Asphaltene deposition. This means that ANS crude has the ability to retain Asphaltene in solution
- Blending crude oil with lower boiling point GTL products results in lowering the Wax Appearance Point of the crude oil.
- Since the lowest pipeline exit temperature is above 50°F, GTL can be transported to Valdez with out the possibility of wax appearance.
- Unlike crude oil, which forms wax over a wide temperature range, due to its wide compositional ranges, Wax formation in the case of GTL is over a narrow temperature range (due to limited number of components), that is, GTL's cloud point and pour point is close to each other. This calls for concern on batch mode of transportation, as there is the possibility of the GTL gelling immediately after wax appearance.
- The result shows that while Asphaltene flocculation and deposition could be a major problem in commingled mode of transportation, wax deposition could affect both batch and commingled-batch modes of transportation.
- Raw GTL has Wax Appearance Temperature as high as 48°F, thus for GTL transportation through the Trans Alaska Pipeline, Lower boiling grades should be synthesized in the North Slope in case of prolonged shut down in winter.

- Since the exit temperature of Trans Alaska Pipeline is 64°F, which is above the wax appearance temperature of the GTL samples considered in this study, and GTL is a possible flocculant of Asphaltene, this shows that batching (batch mode or commingled-batch mode) is a better option to transport GTL through the Trans Alaska Pipeline System, with least risk of solid deposition.

7.2 Recommendations

For future work in this area, the following recommendations are hereby presented for consideration: -

1. A thorough analysis of the interface zone, in a commingled-batch process, to determine its exact composition and characteristics.
2. Evaluation of various options of solid deposition mitigation with a view of determining the best option for GTL/Crude oil transportation through the Trans Alaska Pipeline System.
3. A study of solid deposition on GTL/Crude oil mixtures under dynamic conditions.
4. Further study is needed to determine the optimum slug length to give the minimum interface zone.
5. Effect of solid deposits contamination on GTL quality.
6. For vapor pressure determination, GTL distillation should be done in an airtight apparatus as the light ends are likely to be lost if the distillation is done in a non-airtight chamber.

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Appendix

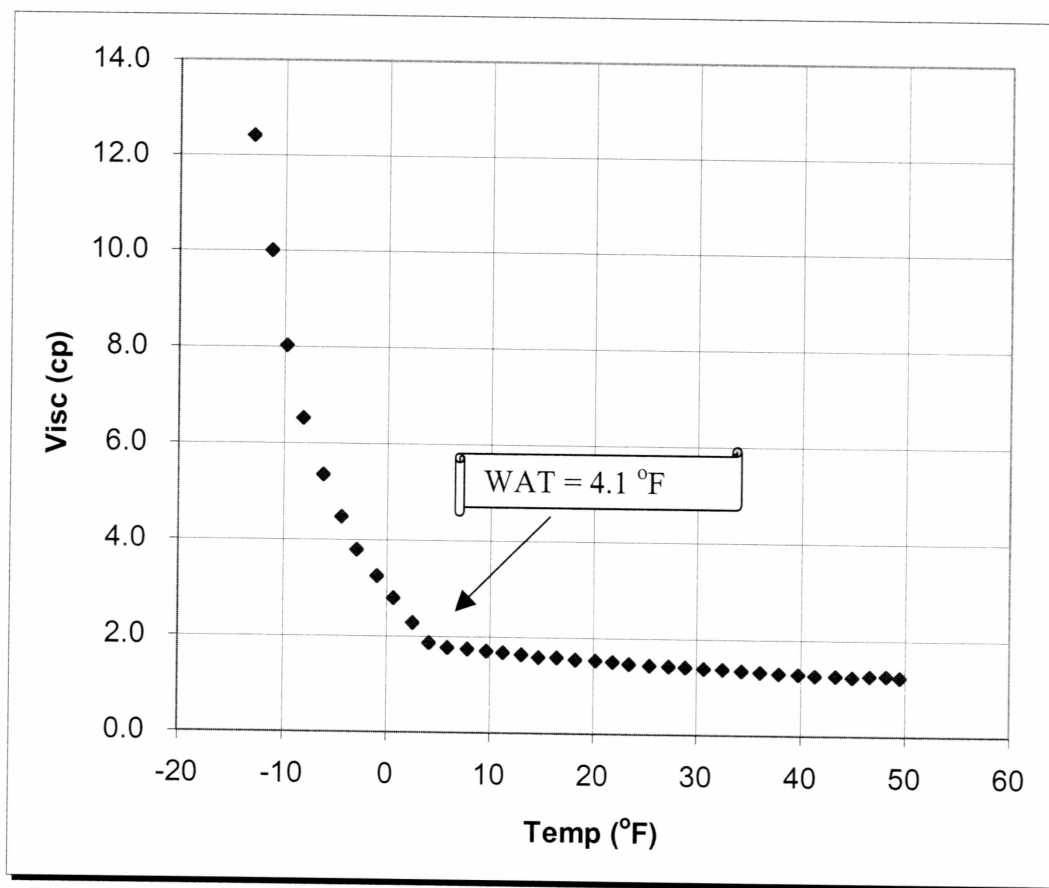


Figure A.1 WAT of 302 GTL Cut

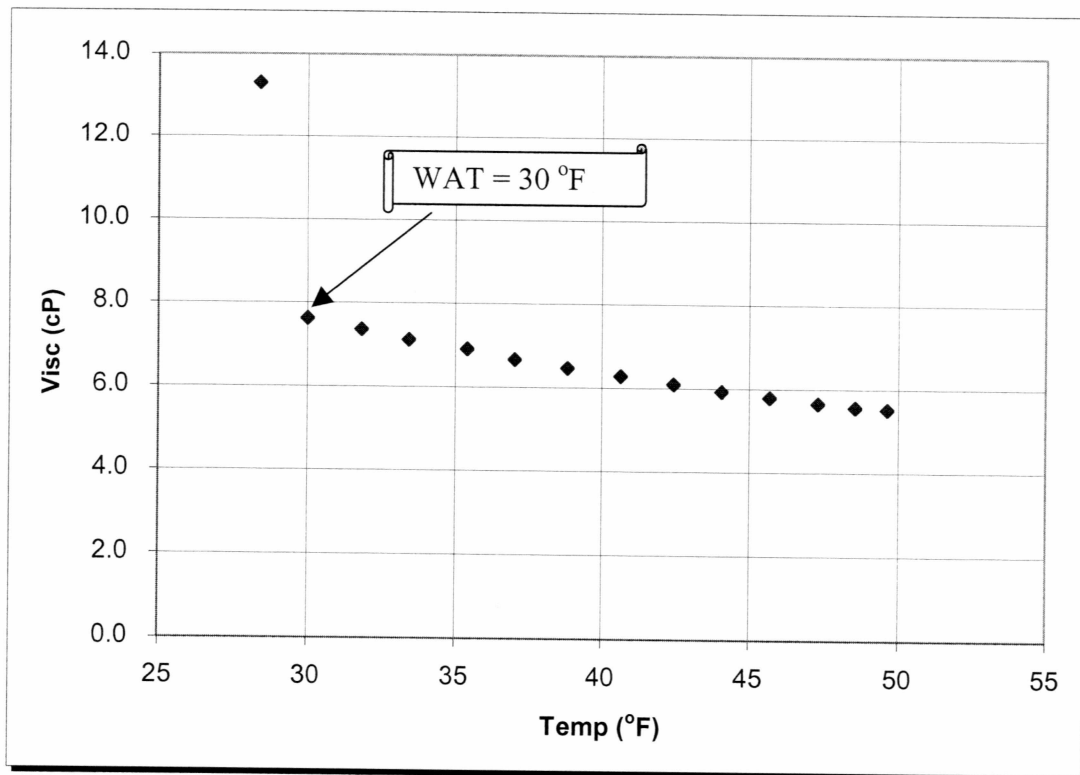


Figure A.2 WAT of FT Diesel

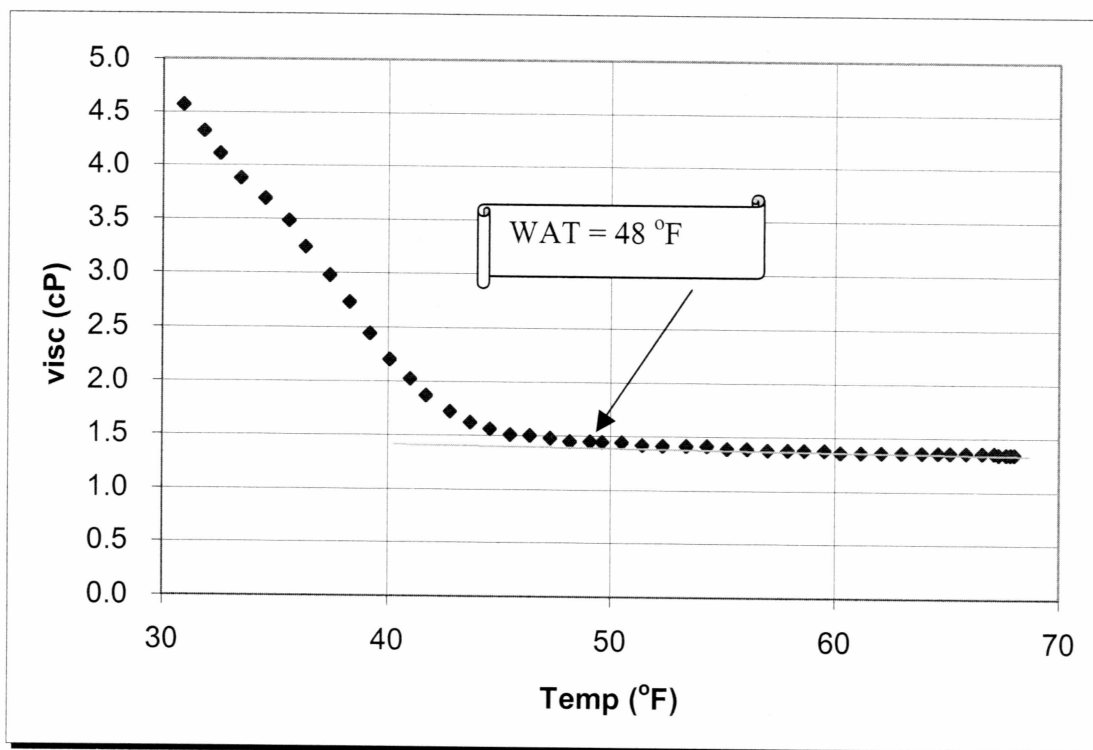


Figure A.3 WAT of Raw GTL

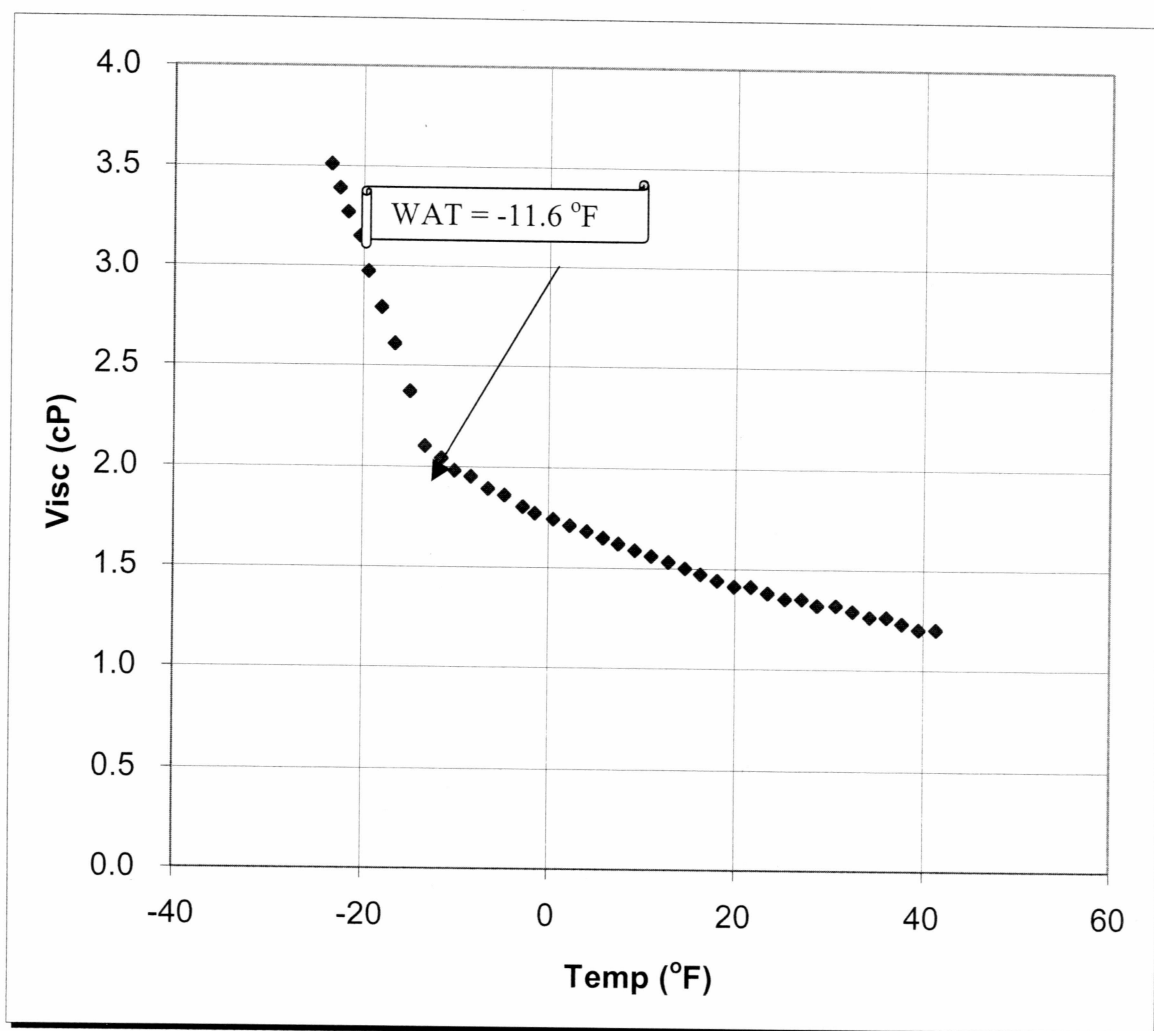


Figure A.4 WAT of 254 GTL Cut

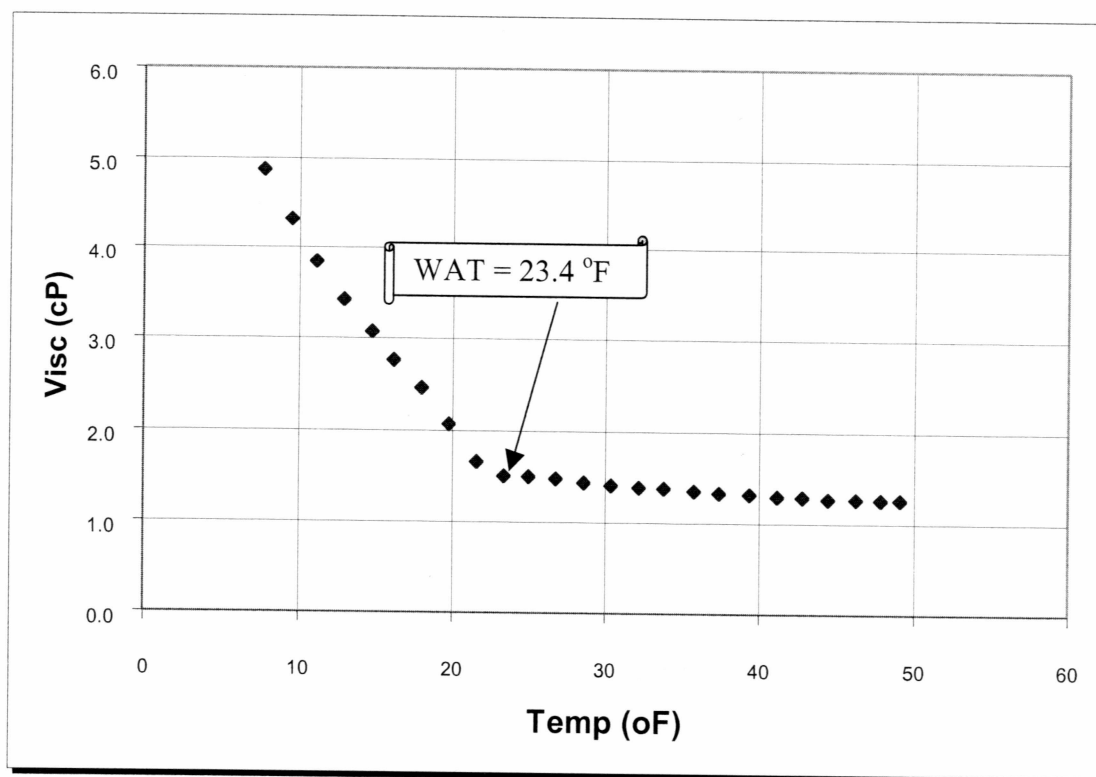


Figure A.5 WAT of 344 GTL Cut

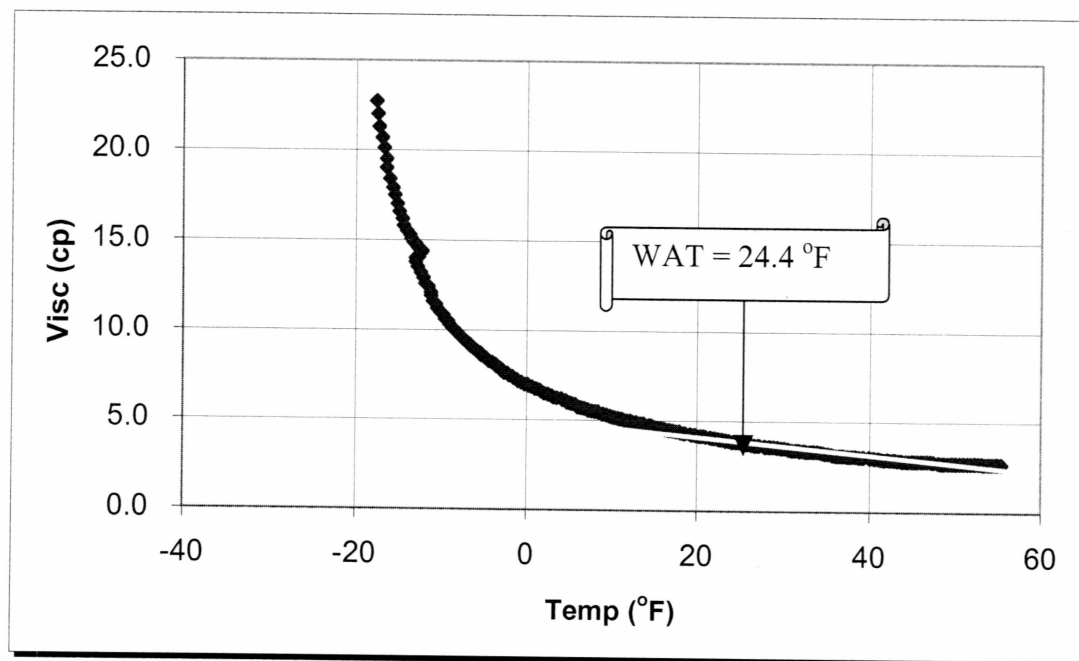


Figure A.6 WAT of 1:1 Crude Oil/302 GTL Cut

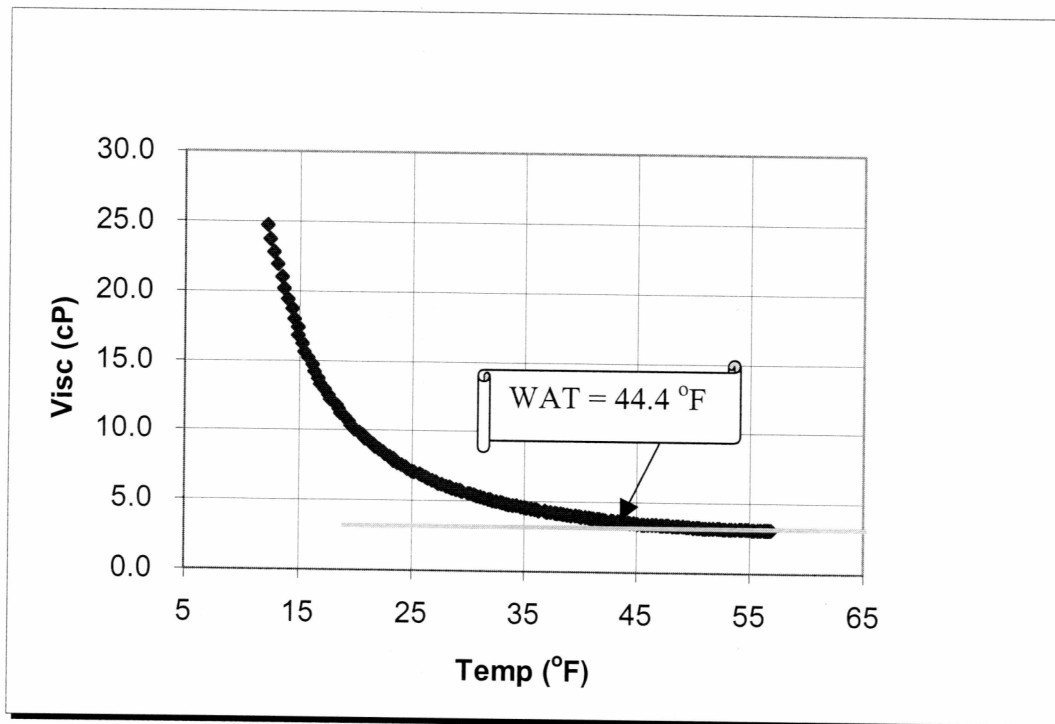


Figure A.7 WAT of 1:1 Crude Oil/ Raw GTL

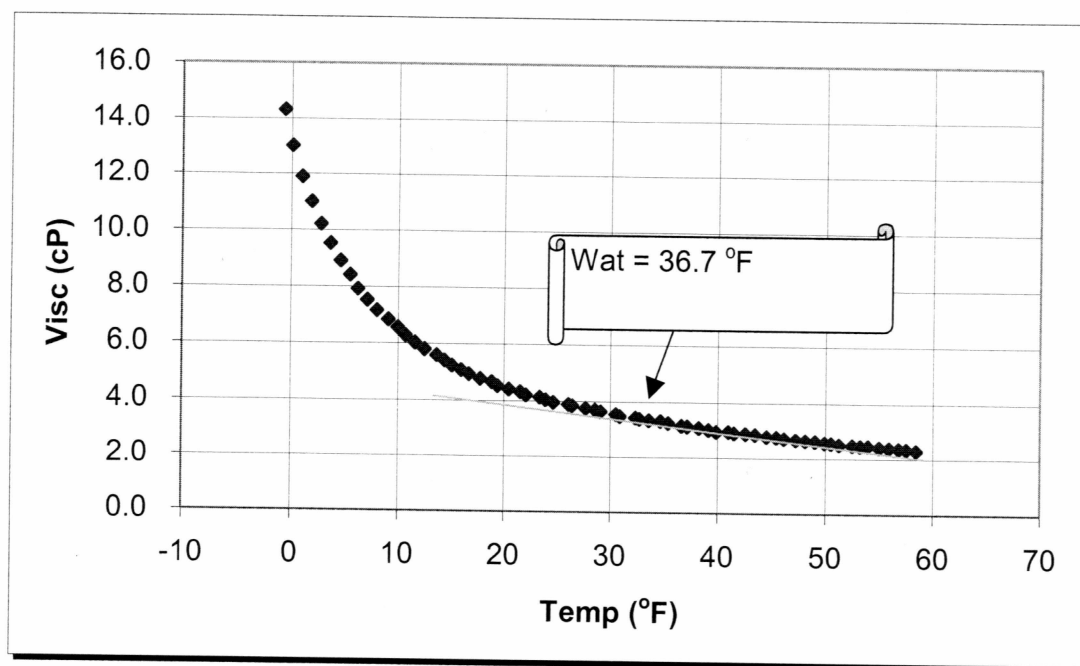


Figure A.8 WAT of 1:1 Crude Oil/344 GTL Cut

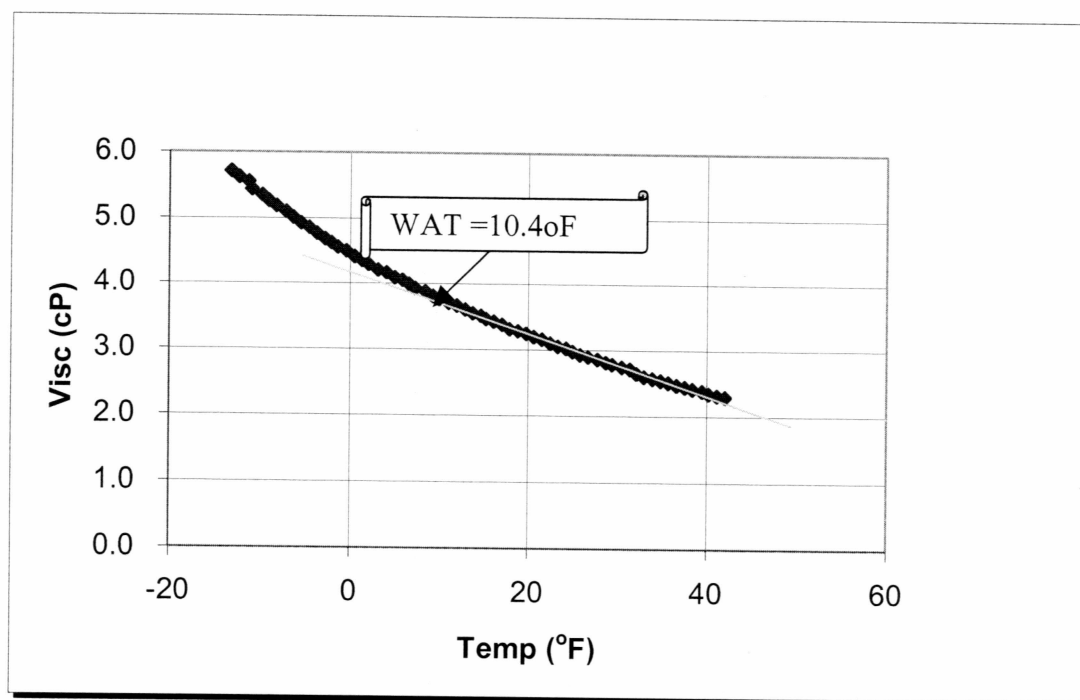


Figure A.9 WAT of 1:1 Crude Oil/254 GTL Cut

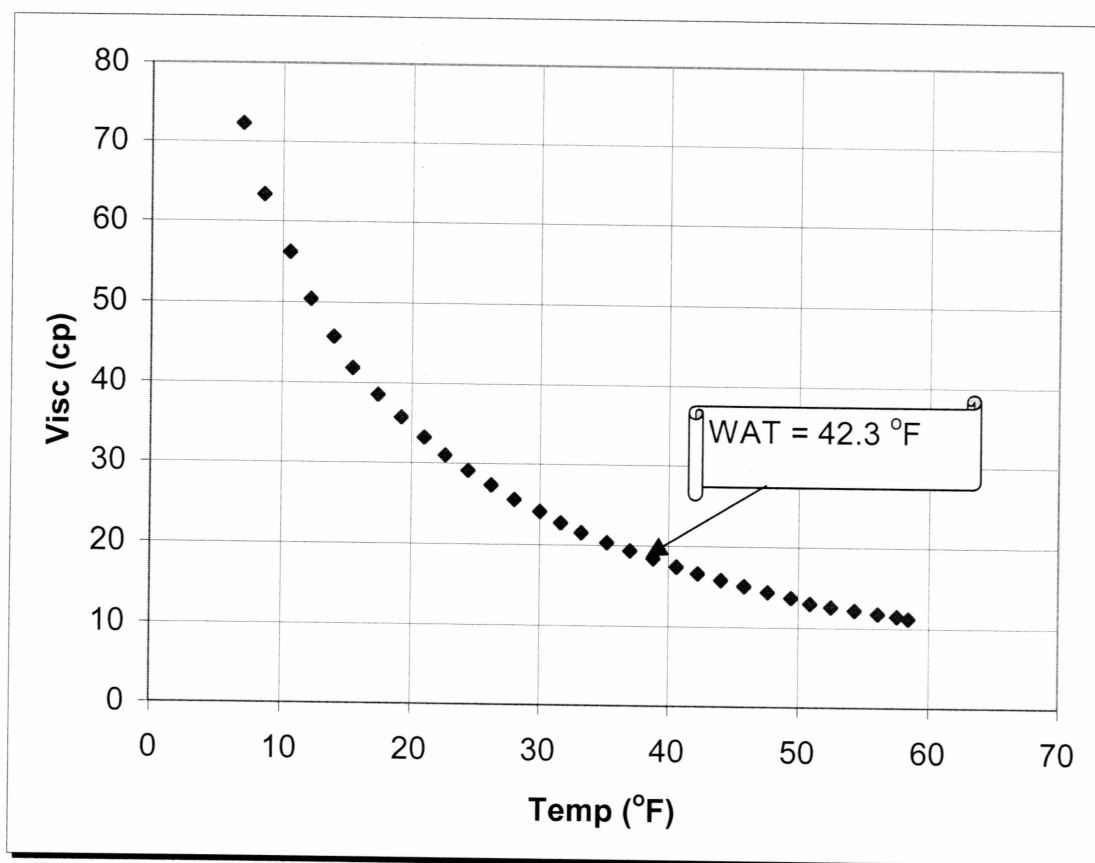


Figure A.10 WAT of 3:1 Crude Oil/FT Diesel

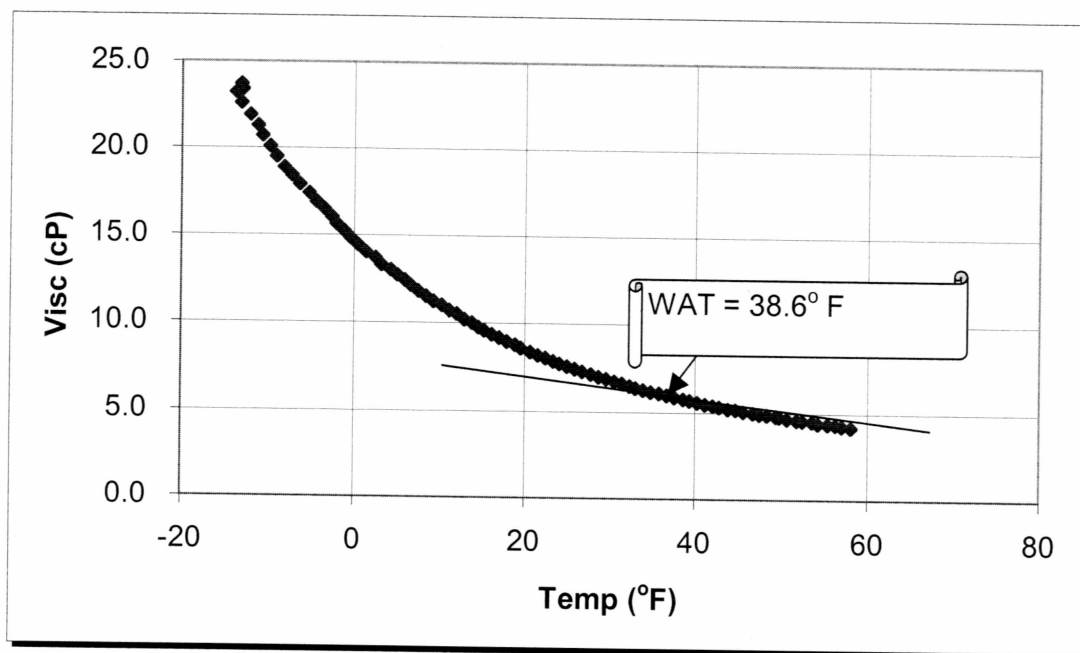


Figure A.11 WAT of 3:1 Crude Oil/254 GTL Cut

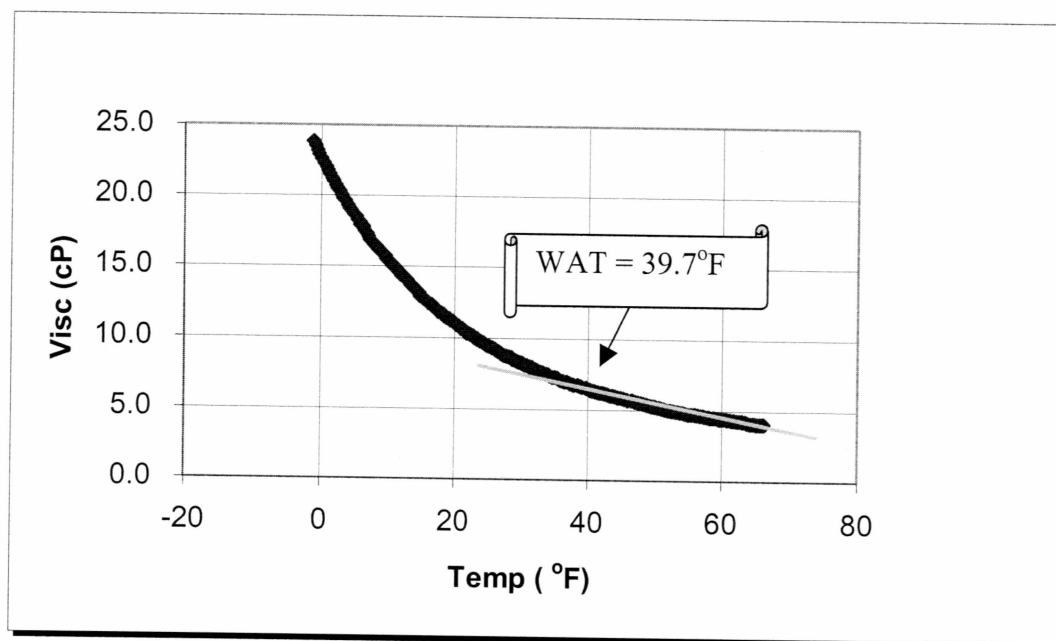


Figure A.12 WAT of 3:1 Crude Oil/302 GTL Cut

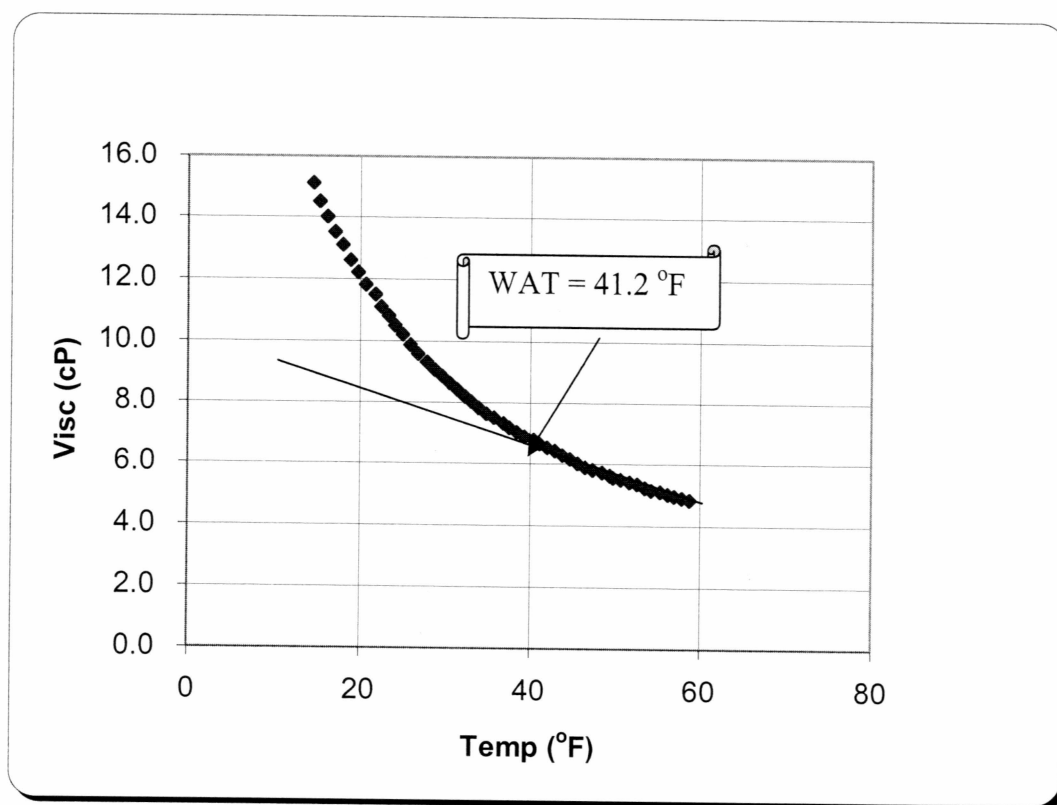


Figure A.13 WAT of 3:1 Crude Oil/344 GTL Cut

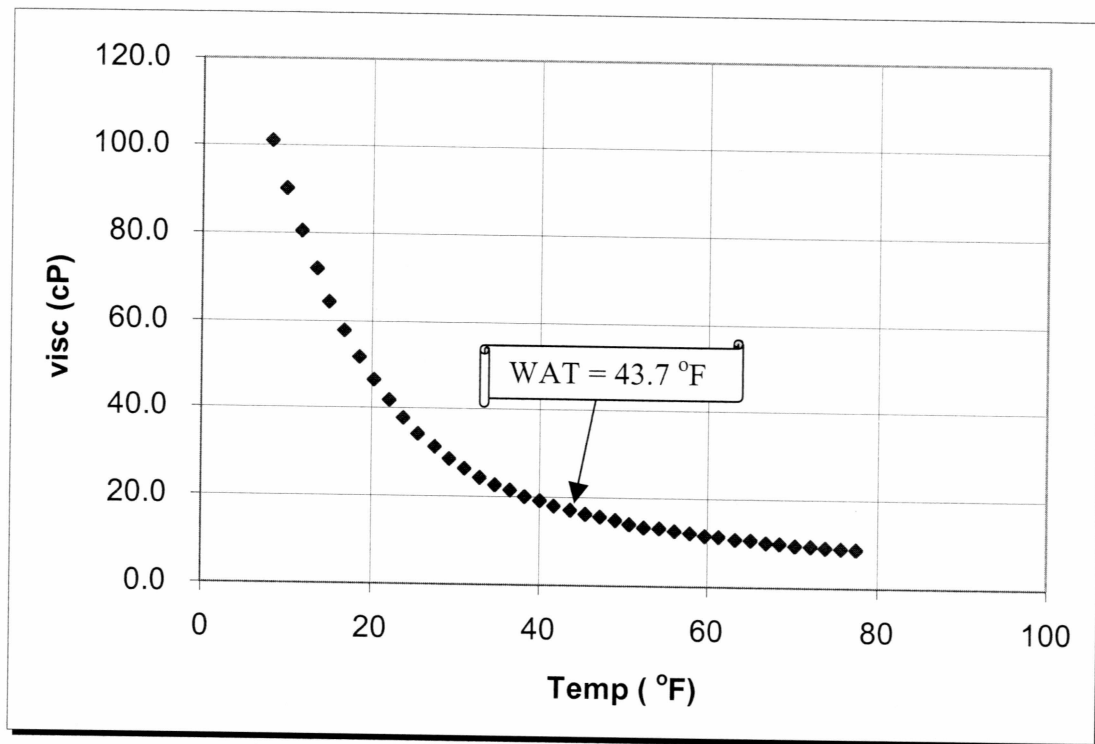


Figure A.14 WAT of Crude Oil